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UTILIZATION OF AMMONIA SUPPLIED TO PEACHES AND PRUNES AT DIFFERENT SEASONS[1]

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NITROGEN fertilization of peaches and prunes in the fruit-growing area of Sutter County, California, has become a well-established practice. Earlier trials and commercial experience have fairly well defined the profitable rates of application for peaches. Responses by prunes are common but not universal in the area. There has been some doubt concerning the relative effectiveness of equal amounts of nitrogen applied at different seasons. This question has now assumed more prominence because of the practice of applying ammonia in the irrigation water as either a summer or a fall treatment. To obtain information on this point, experimental plots of peach and of prune trees were established in 1938.

PEACH EXPERIMENT

A series of plots was laid out in a Paloro peach orchard on Gridley loam, the prevailing soil type in the orchards of the county. The soil is shallower than the best of this series. The orchard was planted in 1924.

Ten plots of 60 trees each were arranged as shown in figure 1. The form of the plots, 4 trees by 15, was adapted to the orchard practices. Trees were planted 20 feet apart each way. Irrigation was by rectangular basins, and all treatments received the same amount of water. Orchard practices were typical of the district. The outside trees—that is, 4 at each end of each plot—served as guards.

METHODS

Nitrogen was applied to all plots except checks at the rate of 1 pound annually per tree. Ammonium sulfate, $(NH_4)_2SO_4$, was put on plots 5 and 10 during the first week in January each year. Anhydrous ammonia, NH_3, was distributed in the first irrigation to plots 1 and 9; in the last irrigation to plots 4 and 6; and half in the first and half in the last irrigation to plots 2 and 7. Plots 3 and 8 were checks. Nitrogen deficiency was so acute in plots 3 and 8 that one application was given them in 1939. The dates of the first irrigation varied from year to year—from May 29 in 1939 to June 25 in 1942. Those of the last irrigation varied from September 8 in 1940 to October 25 in 1939.

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Leaf, shoot, and soil samples were taken at intervals. Leaf samples were composites of 10 leaves per tree, the first basal leaf of full size on shoots of average vigor being selected. Leaves were dried at 60° C. This procedure has been found to give reproducible results, which random sampling of leaves of various ages does not. A somewhat lower variability is obtained if sampling is done early in the morning than if time of day is not considered, but the hour is of less importance than the age of the leaves.

Dormant shoot samples were likewise composites of 10 per tree. One-year wood of moderate vigor was selected. The wood and bark were separated, and each was analyzed. Total nitrogen was determined on the plant samples by

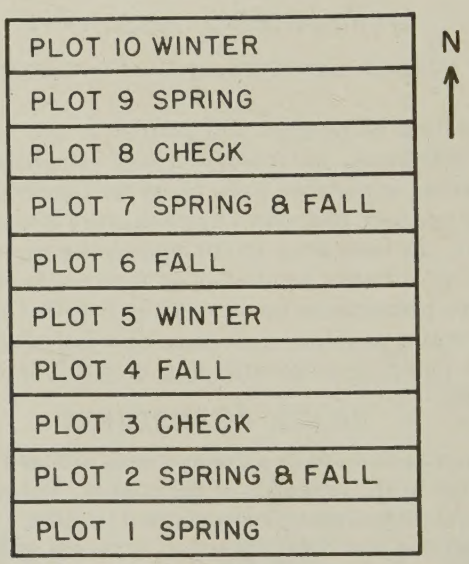

Fig. 1.—Arrangement of peach plots. Each plot is 15 trees long and 4 trees wide.

the official Kjeldahl method. Nitrate in the soil was estimated in 1 : 1 water extracts by the Devarda alloy method. Ammonia analyses were made by the Olsen procedure outlined in Russell (1932).[4] This method proved to be inaccurate for the soils used, and a satisfactory correction has not yet been found. The ammonia data, therefore, are not reported.

Examination of root distribution by plotting permanent roots in trench faces disclosed few roots in the surface foot. The greatest concentration occurred in the second and third feet. Hardpan at about 4 feet limited root penetration to that depth.

Application of NH_3 in the irrigation water was the commercial method of the district. The gas, supplied as a liquid under pressure in steel cylinders, was allowed to bubble through a spreader lying in the irrigation ditch. The rate was controlled by using suitable orifices to give the desired concentration for a known head of water. Samples of the resulting solution were secured at different points to follow distribution. Before the addition of material, analysis

[4] See "Literature Cited" for complete data on citations, referred to in the text by author and date of publication.

showed the irrigation water to contain no ammonia. On May 29, 1939, it had a pH of 7.8, containing 4.30 m.e. of HCO_3^- per liter. After the addition of NH_3 at full rate, the pH increased to 8.4, and the concentration of ammonia below the spreader became 5.50 m.e. per liter. The ammonia concentration at the lower end of the ditch was 5.00; at the head of the basin, plot 9, 5.20; and at the lower end of the same plot, 5.20 m.e. per liter. Where the rate was reduced one half, in plot 7, the concentrations in the same positions were 2.10, 2.70, 2.65, and 2.70 m.e. per liter respectively. These figures indicate lack of completely uniform mixing in the ditch, but an even distribution over the basins, with no appreciable loss by vaporization. Later determinations for the six plots receiving this material showed similar characteristics. The range in concentration was plus or minus 10 per cent between the sample in the ditch and that at the lower end of the basin. Other samples secured from the prune plots likewise showed very good agreement between the samples in the basin, with some deviation from those taken in the ditch.

Preliminary soil sampling to determine the nitrate level, done in June, 1938, showed a mean of 31 $\pm$ 2.8 p.p.m. of NO_3^- on a dry-soil basis in the 0 to 2 foot section, and 13 $\pm$ 1.4 in the 2 to 4 foot. Thereafter, composite samples from six locations in each plot were used; and all the figures in the tables represent such composites.

PRESENTATION OF DATA

The nitrates found in the soil samples are recorded in table 1. As might be expected, the lowest concentration is usually found in the check plots. Evidence of nitrification between the time of application and the next date of sampling is clear, except for the winter application, where leaching into deeper soil has reduced the concentration in the surface foot. Although ammonia analyses are not considered satisfactory, the data secured confirm other experience that NH_4^+ is fixed in the surface soil.

This experiment covered a series of years of more than average rainfall, four of the five being wet, and two having severe floods. The orchard suffered some damage, especially in plot 7. The degree to which root damage following these floods has influenced nitrate concentration by affecting absorbing surface is impossible to evaluate. It may, however, be one reason for the variability shown in these data.

The total nitrogen content of the leaves is reported in table 2. The seasonal curves are typical of those found generally in the literature—namely, a high initial concentration in the spring, which decreases sharply as the leaves mature; a slowly declining percentage through most of the summer; and another drop in the fall. There is a good agreement between duplicate plots, except for plots 2 and 7. The latter is consistently and significantly lower than plot 2. This difference appeared at the outset of the experiment and continued throughout the period of sampling except for a period in 1941. The check plots are significantly lower than any treatment, except the aberrant plot 7. Differences between treated plots, with the same exception, are not significant over the whole period. Absorption following application of NH_3 in the irrigation water has not been demonstrated in less than 3 weeks, and not before the next irrigation following the application. This tends to substantiate the earlier work reported (Proebsting, 1937) and checks with the soil analyses. Although

TABLE 1

NITRATE CONTENT OF SOIL IN PEACH PLOTS FERTILIZED AT DIFFERENT SEASONS, 1938 THROUGH 1942

Date of sampling	0 to 1 foot depth									
	Plot 1, spring	Plot 2, spring and fall	Plot 3, check	Plot 4, fall	Plot 5, winter	Plot 6, fall	Plot 7, spring and fall	Plot 8, check	Plot 9, spring	Plot 10, winter
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
1938:										
June 24	102	94	60	..	..	..	60	40	99	..
July 4	107	84	67	..	..	..	92	84	117	..
July 17	69	87	45	..	..	..	22	37	71	..
Aug. 12	30	24	22	..	..	..	17	21	43	..
Aug. 31	19	32	19	..	..	..	30	26	34	..
Nov. 12	17	55	24	41	16	41	19	16	34	16
Dec. 17	19	22	16	20	15	26	15	11	19	10
1939:										
Mar. 21	14	14	10	32	29	17	15	9	9	20
May 6	17	19	16	31	29	27	27	26	29	30
June 6	61	74	27	15	30	42	27	15	201	25
June 19	68	27	12	6	15	14	16	11	51	16
July 14	47	26	22	29	24	34	22	12	51	21
Aug. 8	15	14	27	20	14	15	15	12	32	10
Sept. 9	17	16	15	16	34	25	12	11	22	11
Nov. 2	16	43	24	24	19	30	20	19	34	21
Dec. 16	30	29	20	30	15	22	17	12	27	29
1940:										
Apr. 13	11	6	10	9	12	16	5	3	5	3
May 11	27	31	25	31	38	58	26	22	22	38
June 18	92	47	17	17	25	32	40	22	65	32
July 29	21	14	11	16	16	17	17	17	35	27
Aug. 12	12	6	5	4	5	11	6	1	9	4
Sept. 21	26	60	22	71	27	77	37	11	38	14
1941:										
May 6	11	37	17	47	57	41	10	7	11	24
May 20	14	22	14	26	26	17	22	17	22	12
June 16	15	16	10	15	61	24	24	26	12	30
June 30	52	38	9	15	15	15	24	15	52	22
July 23	61	12	9	17	10	24	10	9	37	30
Aug. 20	11	7	1	5	4	4	3	3	6	7
Sept. 14	24	22	5	79	39	25	68	22	19	59
Oct. 23	26	196	42	192	140	91	150	47	79	92
1942:										
Apr. 20	17	9	5	7	10	..	..	..	..	..
May 7	27	17	17	21	25	17	12	11	19	19
June 3	40	37	37	33	40	42	22	17	26	37
July 7	88	58	20	25	24	14	67	17	55	15
Aug. 12	21	35	44	39	40	38	21	23	20	35

(Continued on opposite page)

seasonal variations occur as a result of differential timing of applications, the level in all fertilized plots tends to be higher than the level in the checks. With a supply of the order given these trees, greater tissue concentration is maintained until the next annual application. Occasional aberrant samples were found, and these have been reanalyzed to insure that the sample and not the analysis was the variant.

TABLE 1 (*Continued*)

NITRATE CONTENT OF SOIL IN PEACH PLOTS FERTILIZED AT DIFFERENT SEASONS, 1938 THROUGH 1942

Date of sampling	1 to 2 foot depth (1938) or 1 to 3 foot depth (1939 through 1942)									
	Plot 1, spring	Plot 2, spring and fall	Plot 3, check	Plot 4, fall	Plot 5, winter	Plot 6, fall	Plot 7, spring and fall	Plot 8, check	Plot 9, spring	Plot 10, winter
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
1938:										
June 24	17	15	17	..	..	..	12	15	22	..
July 4	62	37	52	..	..	..	42	47	52	..
July 17	20	10	7	..	..	..	6	7	19	..
Aug. 12	22	19	10	..	..	..	8	9	37	..
Aug. 31	26	12	7	..	..	..	9	7	17	..
Nov. 12	12	14	9	9	7	7	9	15	7	7
Dec. 17	12	17	6	9	6	7	7	15	7	6
1939:										
Mar. 21	10	9	10	10	30	7	9	9	7	6
May 6	16	24	24	15	15	12	15	21	14	12
June 6	7	12	12	7	10	12	7	12	15	15
June 19	16	19	5	4	9	6	6	9	10	3
July 14	18	18	6	7	7	5	9	6	9	7
Aug. 8	12	7	10	5	7	12	12	7	11	6
Sept. 9	10	9	4	5	5	3	5	7	10	5
Nov. 2	10	6	5	5	5	3	5	5	5	5
Dec. 16	7	5	5	4	4	3	4	5	5	4
1940:										
Apr. 13	3	3	4	5	6	3	4	3	4	6
May 11	5	6	4	6	6	7	6	6	3	6
June 18	10	17	15	10	17	7	10	7	17	10
July 29	7	6	1	1	3	1	4	3	10	4
Aug. 12	5	9	3	3	4	3	4	5	5	4
Sept. 21	7	6	6	5	7	5	5	3	9	4
1941:										
May 6	11	15	11	5	6	4	5	6	5	4
May 20	6	7	5	6	4	5	4	1	4	5
June 16	12	11	5	5	9	4	6	6	3	4
June 30	6	7	1	5	5	7	6	5	5	9
July 23	17	12	6	3	4	6	5	7	11	5
Aug. 20	3	3	1	3	5	1	1	1	3	3
Sept. 14	4	12	9	9	4	16	14	6	0	4
Oct. 23	35	12	12	14	20	14	20	7	9	12
1942:										
Apr. 20	3	0	1	4	4	..	..	..	..	..
May 7	7	5	3	3	4	1	5	5	5	3
June 3	7	7	9	7	7	5	5	6	5	10
July 7	19	15	16	7	5	6	6	6	10	12
Aug. 12	13	6	20	25	18	20	24	19	16	13

The nitrogen content of dormant wood (table 3) is low. After the first year, the checks tend to run somewhat lower than the fertilized samples; but the differences that develop are not great. Bark samples have a higher nitrogen content and tend to reflect treatment better than wood. There is no evidence of increase in nitrogen content until very shortly before blossoming. This confirms the findings of Aldrich (1931), Batjer, Magness, and Regeimbal (1943),

and others that translocation is negligible while the trees are dormant. The increase just before blossoming noted in table 3 in 1938–39 and, in the prune, in table 8 for March 11, 1942, with no corresponding increase in the wood,

TABLE 2

TOTAL NITROGEN CONTENT OF PEACH LEAVES, 1938 THROUGH 1942
(Dry-weight basis)

Date of sampling	Plot 1, spring	Plot 2, spring and fall	Plot 3, check	Plot 4, fall	Plot 5, winter	Plot 6, fall	Plot 7, spring and fall	Plot 8, check	Plot 9, spring	Plot 10, winter
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1938:										
June 6	2.45	2.57	2.52	2.57	2.43	2.48	2.47	2.59	2.53	2.47
June 24	2.66	2.66	2.56	....	....	....	2.35	2.52	2.64	....
July 9	2.98	3.02	2.62	....	....	....	2.36	2.52	2.95	....
July 19	2.97	2.87	2.66	....	....	....	2.43	2.57	2.93	....
Aug. 12	2.74	2.41	2.37	....	....	....	2.07	2.30	2.35	....
Aug. 31	2.14	2.07	1.87	....	....	....	1.95	2.03	2.24	....
1939:										
Apr. 13	3.47	3.24	2.71	3.08	2.98	3.01	2.86	2.63	3.07	3.00
May 7	2.82	2.65	2.49	2.64	2.54	2.66	2.50	2.48	2.80	2.56
June 6	2.65	2.66	2.38	2.63	2.52	2.61	2.30	2.32	2.52	2.57
June 19	2.89	2.68	2.30	2.67	2.38	2.66	2.35	2.32	2.66	2.66
July 14	3.06	2.94	2.26	2.85	2.76	2.96	2.66	2.57	3.07	2.80
Aug. 8	3.01	2.84	2.38	2.77	2.79	2.80	2.49	2.62	3.07	2.71
Sept. 9	2.79	2.65	2.36	2.47	2.46	2.56	2.39	2.50	2.67	2.47
1940:										
Apr. 13	3.76	3.60	3.46	3.76	3.94	3.86	3.54	3.45	3.62	3.82
May 11	2.86	3.10	2.94	3.17	3.27	3.24	2.82	2.88	3.14	3.30
June 18	2.68	2.62	2.32	2.38	2.64	2.60	2.38	2.23	2.22	2.46
July 29	2.79	2.76	2.19	2.62	2.68	2.56	2.26	2.18	2.78	2.73
Aug. 12	2.58	2.66	2.26	2.56	2.43	2.31	2.26	2.01	2.60	2.50
Sept. 21	2.34	2.40	2.00	2.14	2.03	2.18	1.88	1.79	2.20	2.22
1941:										
Apr. 19	3.19	2.94	2.88	2.76	3.36	3.32	3.28	2.78	3.42	3.45
May 5	3.08	2.96	2.82	3.17	3.62	3.34	3.23	3.28	3.34	3.76
May 20	3.02	3.23	2.90	3.47	3.51	3.40	3.29	3.07	3.22	3.40
June 16	2.62	2.54	2.32	2.78	2.99	2.78	2.61	2.61	2.56	2.39
June 30	2.45	2.67	2.40	2.54	3.10	2.49	2.46	2.71	2.78	3.15
July 23	2.99	2.69	2.49	2.28	2.86	2.48	2.60	2.39	3.13	2.87
Aug. 20	2.68	2.59	2.14	2.24	2.49	2.27	2.59	2.20	2.65	2.79
Sept. 15	2.12	2.36	1.85	1.92	2.13	1.98	1.98	1.93	2.05	2.43
1942:										
May 7	3.24	3.26	3.06	3.31	3.51	3.63	3.15	2.90	3.30	3.72
June 3	2.51	3.16	2.67	3.23	2.73	3.18	2.84	3.07	2.70	3.07
July 7	2.28	2.48	2.16	2.36	2.36	2.56	2.41	2.18	2.46	2.71
Aug. 12	2.14	2.15	1.85	1.89	2.26	1.84	1.91	1.86	2.20	2.26

suggests some translocation in the bark before the beginning of an appreciable transpiration stream in the spring.

The yields are given in table 4. The 1938 season can be considered as preliminary, since only four plots received any nitrogen before harvest, and two of those only half of their seasonal total. The sole influence possible from such an application as was given would be on the size of individual fruits. Nothing in the data suggests that there was any such effect.

TABLE 3

TOTAL NITROGEN IN BARK AND WOOD OF ONE-YEAR-OLD PEACH SHOOTS, 1938–39 THROUGH 1941–42

(Dry-weight basis)

Date of sampling	Nitrogen in bark									
	Plot 1, spring	Plot 2, spring and fall	Plot 3, check	Plot 4, fall	Plot 5, winter	Plot 6, fall	Plot 7, spring and fall	Plot 8, check	Plot 9, spring	Plot 10, winter
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1938–39:										
Nov. 12	1.89	1.67	1.54	1.64	1.38	1.48	1.68	1.65	1.77	1.56
Dec. 17	2.07	1.96	1.93	2.10	1.86	2.08	1.96	1.87	2.05	1.98
Jan. 9	1.86	1.62	1.47	1.58	1.48	1.59	1.70	1.75	1.84	1.70
Feb. 17	1.90	1.77	1.52	1.70	1.60	1.62	1.64	1.66	1.83	1.66
Mar. 21	2.50	2.35	2.12	2.26	2.27	2.26	2.28	2.25	2.45	2.32
1939–40:										
Nov. 2	1.99	1.94	1.96	1.88	1.77	1.84	1.77	1.89	1.88	1.86
Dec. 16	2.12	1.96	2.01	1.87	1.90	1.92	1.85	1.78	2.08	1.88
Jan. 12	2.18	2.03	1.95	1.92	1.98	1.94	1.94	2.03	2.04	2.10
Feb. 22	2.23	2.25	2.19	2.16	2.04	2.10	2.04	2.14	2.16	2.14
1940–41:										
Nov. 9	1.82	1.76	1.70	1.93	1.82	1.84	1.80	1.74	1.82	1.98
Feb. 22	1.84	1.91	1.70	1.78	1.75	1.78	1.75	1.78	1.94	1.93
1941–42:										
Oct. 28	1.56	1.45	1.55	1.45	1.35	1.54	1.53	1.34	1.72	1.49
Dec. 8	1.52	1.70	1.47	1.66	1.57	1.79	1.84	1.58	1.86	1.82
Feb. 13	1.70	1.62	1.34	1.51	1.57	1.35	1.75	1.43	1.85	1.53

Date of sampling	Nitrogen in wood									
	Plot 1, spring	Plot 2, spring and fall	Plot 3, check	Plot 4, fall	Plot 5, winter	Plot 6, fall	Plot 7, spring and fall	Plot 8, check	Plot 9, spring	Plot 10, winter
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1938–39:										
Nov. 12	0.47	0.42	0.38	0.46	0.35	0.39	0.46	0.47	0.47	0.43
Dec. 17	0.53	0.53	0.49	0.48	0.47	0.51	0.56	0.45	0.55	0.47
Jan. 9	0.55	0.52	0.45	0.48	0.44	0.47	0.51	0.50	0.52	0.46
Feb. 17	0.48	0.48	0.43	0.46	0.43	0.48	0.48	0.52	0.53	0.47
Mar. 21	0.48	0.48	0.44	0.45	0.46	0.48	0.48	0.43	0.52	0.48
1939–40:										
Nov. 2	0.76	0.67	0.54	0.63	0.54	0.68	0.66	0.68	0.75	0.60
Dec. 16	0.45	0.42	0.48	0.42	0.40	0.45	0.42	0.43	0.45	0.44
Jan. 12	0.52	0.54	0.48	0.50	0.50	0.52	0.50	0.52	0.50	0.52
Feb. 22	0.43	0.49	0.43	0.42	0.42	0.47	0.45	0.48	0.48	0.46
1940–41:										
Nov. 9	0.42	0.44	0.42	0.46	0.45	0.44	0.42	0.42	0.51	0.50
Feb. 22	0.34	0.36	0.32	0.36	0.36	0.37	0.38	0.36	0.41	0.41
1941–42:										
Oct. 28	0.50	0.48	0.44	0.53	0.52	0.52	0.47	0.46	0.59	0.63
Dec. 8	....	....	....	....	....	....	....	....	....	....
Feb. 13	0.53	0.48	0.38	0.48	0.48	0.45	0.51	0.45	0.53	0.49

The plots that received $(NH_4)_2SO_4$ in the winter (nos. 5 and 10), those that had NH_3 in the spring (nos. 1 and 9) and no. 2, which had split applications, clearly outyielded the checks, and showed no significant differences among them. The fall plots (nos. 4 and 6) take an intermediate position. Plot 4 is not significantly better than its adjacent check, plot 3; but plot 6 is better than plot 8. Excluding 1938, when neither had been treated, the combination of plots 4 and 6 shows odds of 40:1 that it outyields the checks. Although inherent differences are suggested in the 1938 data, plot 7 being low and 10 high, only plot 7 proved to be seriously aberrant. This plot (no. 7) outyielded the check plot each year after 1938, but not significantly, and was lower than the other fertilized plots on the average. Taken in conjunction with the low nitrogen content of the leaves, noted above, these facts would suggest caution

TABLE 4

YIELD OF MARKETABLE PEACHES PER TREE, 1938 THROUGH 1942

Year	Plot 1, spring	Plot 2, spring and fall	Plot 3, check	Plot 4, fall	Plot 5, winter	Plot 6, fall	Plot 7, spring and fall	Plot 8, check	Plot 9, spring	Plot 10, winter
	pounds	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*
1938	194±5.9	184±6.6	193±6.5	178±6.0	171±9.4	162±8.1	139±8.9	169±8.7	201±7.9	236±8.7
1939	270±8.2	292±6.9	239±6.9	265±6.7	275±5.6	245±6.4	179±6.8	152±6.4	245±9.2	296±5.4
1940	198±5.2	190±6.2	163±5.0	181±3.7	203±4.5	186±6.1	148±4.8	122±3.8	180±5.8	193±4.7
1941	159±4.4	122±3.7	101±3.6	96±3.4	133±4.4	106±3.7	116±3.1	103±4.1	131±4.3	117±3.6
1942	164±5.5	180±5.4	150±3.1	146±3.7	185±5.7	151±5.4	120±3.5	105±3.8	185±3.9	205±4.8

in the use of data from this plot. Since there was no delay in maturity in any plot, apparently the rate of application was not excessive.

The phosphorus content of the plant samples was also determined. The wood and bark samples showed no regular relation. The leaves, with few exceptions, gave the usual inverse relation reported earlier by Proebsting and Kinman (1933) and substantiated by others. Plot 7, which had a low nitrogen content even though fertilized, had a high phosphorus content.

PRUNE EXPERIMENT

A series of plots of prune trees was established in October, 1938, following the same general plan described for peaches. The trees were planted in 1918 on Gridley clay loam 20 feet apart each way. Ten plots of 20 trees each were arranged as shown in figure 2. A guard row surrounded the block, and two guard rows separated the two sets of replications. Irrigation was by rectangular basins, and all received the same irrigation treatment. The time and rate of application of nitrogen followed the same scheme outlined for peaches. The first irrigation varied in time from May in 1939 to July in 1942; the last from late July to August. Winter applications of $(NH_4)_2SO_4$ were made early in January each year except 1943, when it was delayed until March 3.

Data were collected for three years on the percentage set of the blossoms in the various plots. These figures are the averages of 10 branches in each plot, each branch being taken from a different tree. The blossoms were counted, and the fruits reaching maturity on the same branches were counted just before harvest. Variability was high; and the results are not considered significant,

although the winter plots average the highest throughout and may approach significance. The behavior of these trees in this respect differs from general experience with trees in low nitrogen status. Obviously, percentage set is only one factor concerned; the same number of fruits might be secured by a high percentage set with light bloom and a low percentage set with heavy bloom.

Drying ratios were secured for the 1940 and 1941 crops. Samples of about 500 pounds fresh weight were taken from each plot and dehydrated in the University dehydrater. Drying ratios varied from 2.05 : 1 to 2.36 : 1 in 1940 and from 1.87 : 1 to 2.53 : 1 in 1941. This variation was random. For example, both of the extremes came from winter-fertilized plots in 1941. Factors other than the fertilization treatment have dominated this relation.

Each lot of fruit was graded after drying; and the size distribution, percentage of culls, and specific gravity for each lot are reported in table 5. Size

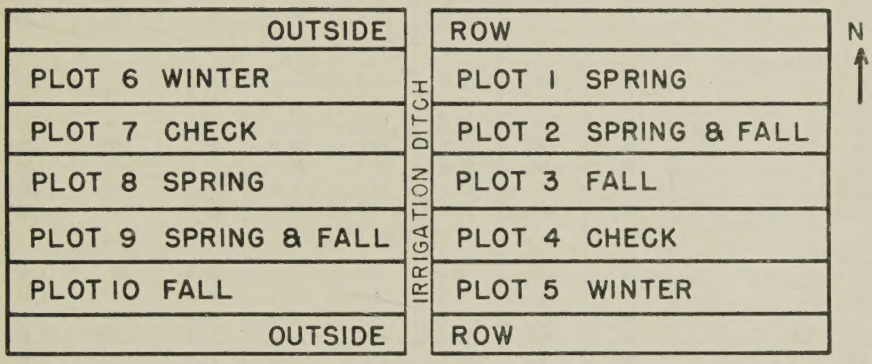

Fig. 2.—Arrangement of prune plots. Each plot is 10 trees long and 2 trees wide.

distribution seems to be principally a matter of number of fruits per tree, according to the data of Hendrickson and Veihmeyer (1942). These data fall in line with such an interpretation. The culls in 1940 consisted largely of split fruit, a condition general in the district in that year. Those in 1941 were largely fruits damaged by brown rot. Treatment has not affected the size of fruit significantly in this experiment.

The specific gravity was determined by weighing samples in air and in xylene, in an effort to find a short method of estimating quality. This method has been explored over a period of ten years by Hendrickson,[5] who has recently dismissed it except as a measure indicating the texture of the flesh.

Yield records (table 6) were secured for each of the five years. Thus far there was little evidence of response, despite the better tree condition produced by the nitrogen. There was a pronounced difference in the color of foliage and the amount of new growth between fertilized and check trees. Other factors have dominated the development of fruit; and even in 1943, the year of maximum crop, when the greatest response would be expected, differences are neither great nor consistent. Evidently, despite a relatively low supply of nitrogen, this material is not limiting in this orchard. The difference in behavior between prunes and peaches in this soil and district confirms the gen-

[5] Hendrickson, A. H. Unpublished data.

TABLE 5

PER CENT OF DRY WEIGHT IN EACH SIZE, NUMBER OF DRIED PRUNES PER POUND, PER CENT CULLS, AND SPECIFIC GRAVITY OF DRIED PRUNES

Plot no., treatment, and screen no.	Size of fruit		Percentage in each size		Culls		Specific gravity	
	1940	1941	1940	1941	1940	1941	1940	1941
	number per pound	*number per pound*	*per cent*	*per cent*	*per cent*	*per cent*		
No. 1, spring:								
28	103	102	1.7	3.8	....	38.6	....	1.27
30	79	78	5.6	9.5	....	28.9	....	1.30
32	56	65	15.1	16.0	21.5	27.0	1.27	1.28
34	49	55	22.4	25.2	19.7	23.0	1.31	1.30
36	44	50	25.0	26.5	19.2	16.5	1.28	1.23
38	41	45	19.8	16.5	11.4	23.4	1.27	1.23
End	37	42	10.3	2.4	16.1	42.4	1.27	1.20
No. 2, spring and fall:								
28	104	103	0.8	2.5	....	38.5	....	1.25
30	81	81	3.7	6.9	....	28.8	....	1.29
32	56	66	12.4	15.3	20.7	26.1	1.30	1.28
34	49	56	21.8	24.6	23.0	24.7	1.31	1.29
36	45	48	26.9	27.0	23.8	9.5	1.28	1.23
38	40	45	21.1	19.9	22.6	27.6	1.27	1.26
End	36	38	13.2	3.6	15.4	31.8	1.29	1.23
No. 3, fall:								
28	99	97	0.4	2.7	....	29.9	....	1.29
30	82	81	1.6	4.8	....	23.4	....	1.31
32	58	65	7.1	8.7	16.4	14.2	1.30	1.31
34	48	54	14.6	15.9	14.7	17.5	1.28	1.32
36	44	45	26.5	26.9	13.8	11.4	1.28	1.31
38	38	43	26.9	33.0	11.7	32.4	1.29	1.33
End	33	34	22.9	8.0	13.8	20.3	1.29	1.31
No. 4, check:								
28	103	106	0.8	2.5	....	20.1	....	1.28
30	79	77	3.3	5.6	....	21.8	....	1.31
32	56	62	9.4	10.7	12.8	26.0	1.30	1.34
34	48	54	18.9	20.2	8.8	24.5	1.30	1.32
36	42	47	27.0	29.4	9.5	18.5	1.28	1.32
38	38	41	24.2	26.2	12.7	13.6	1.31	1.32
End	35	37	16.4	5.4	9.7	24.1	1.29	1.32
No. 5, winter:								
28	109	111	1.7	13.0	....	13.7	....	1.20
30	90	91	6.1	20.7	....	22.0	....	1.24
32	56	75	12.6	23.9	18.4	22.8	1.29	1.21
34	48	64	22.2	21.0	12.3	23.6	1.29	1.20
36	45	59	24.4	13.6	7.8	36.4	1.27	1.21
38	40	49	20.4	6.7	6.8	38.9	1.29	1.15
End	37	45	12.6	1.1	4.9	41.1	1.28	1.00
No. 6, winter:								
28	112	117	0.8	3.1	....	43.1	....	1.20
30	82	82	1.2	6.3	....	26.6	....	1.19
32	60	68	6.2	15.1	15.8	45.5	1.29	1.23
34	52	57	12.9	22.2	22.2	22.5	1.29	1.26
36	45	49	21.6	26.6	14.8	25.9	1.26	1.17
38	40	46	25.7	24.3	14.5	27.1	1.26	1.22
End	35	40	31.5	2.5	17.2	31.6	1.28	1.19

(Continued on opposite page)

TABLE 5 (*Continued*)

PER CENT OF DRY WEIGHT IN EACH SIZE, NUMBER OF DRIED PRUNES PER POUND, PER CENT CULLS, AND SPECIFIC GRAVITY OF DRIED PRUNES

Plot no., treatment, and screen no.	Size of fruit		Percentage in each size		Culls		Specific gravity	
	1940	1941	1940	1941	1940	1941	1940	1941
	number per pound	*number per pound*	*per cent*	*per cent*	*per cent*	*per cent*		
No. 7, check:								
28	..	99	0	0.6	....	....	....	1.18
30	76	76	1.3	1.5	....	33.6	....	1.21
32	55	64	3.8	4.0	10.8	23.8	1.31	1.21
34	49	54	9.3	12.9	10.8	19.9	1.33	1.26
36	42	46	20.4	26.0	8.4	19.7	1.31	1.22
38	38	41	29.0	38.8	9.7	15.3	1.30	1.24
End	32	35	36.0	16.1	13.2	17.9	1.31	1.24
No. 8, spring:								
28	..	99	0	0.7	....	....	....	1.27
30	78	77	1.1	2.2	....	27.3	....	1.29
32	57	61	4.3	5.3	18.5	26.5	1.26	1.28
34	49	53	12.0	12.2	16.8	28.2	1.28	1.28
36	43	46	23.9	28.0	17.2	22.5	1.29	1.30
38	38	40	28.3	38.7	14.4	19.2	1.28	1.30
End	34	34	30.4	12.9	10.0	18.6	1.29	1.28
No. 9, spring and fall:								
28	100	102	1.6	2.1	....	15.9	....	1.24
30	78	76	4.3	5.7	....	19.4	....	1.28
32	61	67	11.8	13.3	30.2	24.7	1.28	1.31
34	50	58	20.1	22.9	36.5	19.4	1.30	1.30
36	43	47	28.4	29.9	26.4	13.9	1.29	1.23
38	40	42	19.7	22.5	25.7	9.3	1.31	1.28
End	35	35	14.2	3.5	20.7	18.8	1.29	1.22
No. 10, fall:								
28	102	105	1.1	1.4	....	20.9	....	1.27
30	77	76	2.5	4.3	....	18.4	....	1.32
32	55	64	7.4	19.1	27.9	9.6	1.32	1.30
34	49	50	15.1	19.2	32.9	9.4	1.31	1.31
36	45	47	27.0	27.9	26.6	10.8	1.28	1.31
38	40	42	27.7	23.0	22.5	15.6	1.27	1.31
End	35	35	19.3	5.1	25.5	23.3	1.27	1.31

TABLE 6

YIELDS OF PRUNES IN FRESH WEIGHT, PER TREE, 1939 THROUGH 1943

Year	Plot 1, spring	Plot 2, spring and fall	Plot 3, fall	Plot 4, check	Plot 5, winter	Plot 6, winter	Plot 7, check	Plot 8, spring	Plot 9, spring and fall	Plot 10, fall
	pounds	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*
1939	24±3.4	28±3.6	19±4.5	36±4.5	33±4.6	60±5.6	54±5.2	53±5.4	53±5.9	51±4.2
1940	167±7.8	120±9.4	113±8.7	112±9.9	164±10.4	151±6.7	80±4.6	108±6.1	110±6.3	105±6.1
1941	182±10.6	155±8.7	156±11.4	161±9.3	212±10.4	138±7.5	115±9.6	112±5.9	127±9.6	134±8.5
1942	75±6.7	68±7.6	89±7.8	65±5.3	59±6.9	66±4.3	58±4.6	54±4.2	72±7.2	86±5.1
1943	271±15.5	224±16.9	216±12.8	221±11.4	244±15.5	320±16.8	262±21.0	229±10.1	194±11.4	252±12.8

TABLE 7

TOTAL NITROGEN CONTENT OF PRUNE LEAVES, 1939 THROUGH 1943
(Dry-weight basis)

Date of sampling	Plot 1, spring	Plot 2, spring and fall	Plot 3, fall	Plot 4, check	Plot 5, winter	Plot 6, winter	Plot 7, check	Plot 8, spring	Plot 9, spring and fall	Plot 10, fall
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1939:										
May 6	2.31	2.24	2.29	2.28	2.45	2.39	2.22	2.25	2.27	2.20
June 2	2.04	2.01	1.98	2.02	2.29	2.34	2.02	2.00	2.01	1.98
June 19	1.93	1.86	1.77	1.73	2.16	2.16	1.79	1.89	1.86	1.80
July 5	1.83	1.80	1.69	1.69	2.02	2.06	1.72	1.86	1.92	1.69
Aug. 8	1.96	1.87	1.58	1.53	1.93	1.96	1.61	1.79	1.91	1.52
Sept. 9	1.83	1.61	1.45	1.39	1.79	1.88	1.57	1.72	1.73	1.47
1940:										
June 24	2.12	2.00	2.04	1.69	2.41	2.63	1.78	1.97	1.99	1.92
July 17	2.13	1.71	1.66	1.57	2.10	2.18	1.56	1.84	1.88	1.64
Aug. 1	1.92	1.86	1.66	1.49	2.00	2.08	1.54	1.91	1.88	1.88
Sept. 21	1.72	1.64	1.52	1.29	1.71	1.78	1.46	1.70	1.48	1.50
1941:										
May 6	2.14	2.18	2.23	1.95	2.44	2.42	2.01	2.15	2.18	2.26
May 20	2.26	2.35	2.34	2.02	2.60	2.58	2.08	2.22	2.24	2.22
June 25	1.97	1.78	1.78	1.69	2.11	2.12	1.83	1.82	1.90	1.81
July 15	1.89	1.84	1.84	1.67	2.14	2.12	1.78	1.94	1.78	1.70
July 23	2.02	1.98	1.94	1.79	2.12	2.17	1.76	2.10	1.99	1.87
Aug. 20	1.86	1.78	1.72	1.58	1.92	1.82	1.50	1.88	1.73	1.70
Sept. 15	1.54	1.46	1.48	1.47	1.60	1.60	1.37	1.38	1.53	1.47
1942:										
May 7	2.80	2.65	2.49	2.35	3.02	2.52	2.61	2.65	2.60	2.56
June 3	2.08	1.96	1.95	1.87	2.23	2.35	2.01	2.27	2.16	1.95
July 7	1.57	1.60	1.75	1.66	1.90	1.89	1.60	1.65	1.69	1.58
Aug. 12	1.67	1.68	1.63	1.55	1.73	1.78	1.53	1.69	1.76	1.74
1943:										
May 5	2.38	2.34	2.34	2.27	2.48	2.68	2.20	2.28	2.49	2.38
June 18	2.10	2.14	2.10	1.88	2.13	2.23	1.98	2.20	2.14	2.17

TABLE 8

TOTAL NITROGEN CONTENT OF BARK FROM PRUNE SHOOTS, 1939 THROUGH 1942
(Dry-weight basis)

Date of sampling	Plot 1, spring	Plot 2, spring and fall	Plot 3, fall	Plot 4, check	Plot 5, winter	Plot 6. winter	Plot 7, check	Plot 8, spring	Plot 9, spring and fall	Plot 10. fall
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1939:										
Jan. 4	1.42	1.47	1.40	1.51	1.54	1.56	1.60	1.56	1.47	1.44
Feb. 14	1.34	1.27	1.30	1.31	1.33	1.41	1.47	1.53	1.33	1.35
1939–40:										
Nov. 24	1.64	1.63	1.38	1.39	1.56	1.63	1.41	1.65	1.57	1.44
Jan. 12	1.68	1.60	1.40	1.40	1.60	1.79	1.49	1.66	1.66	1.48
1940–41:										
Nov. 9	1.55	1.55	1.48	1.37	1.51	1.67	1.44	1.55	1.43	1.47
Feb. 1	1.80	1.71	1.64	1.68	1.68	1.63	1.56	1.68	1.70	1.57
1941–42:										
Oct. 28	1.45	1.40	1.34	1.35	1.48	1.52	1.35	1.46	1.29	1.19
Dec. 3	1.42	1.33	1.31	1.31	1.48	1.44	1.30	1.39	1.39	1.36
Mar. 11	1.68	1.58	1.61	1.58	1.60	1.74	1.44	1.67	1.65	1.65

TABLE 9

NITRATE CONTENT OF SOIL IN PRUNE PLOTS FERTILIZED AT DIFFERENT SEASONS, 1939 THROUGH 1942

(Dry-soil basis)

Date of sampling	Plot 1, spring	Plot 2, spring and fall	Plot 3, fall	Plot 4, check	Plot 5, winter	Plot 6, winter	Plot 7, check	Plot 8, spring	Plot 9, spring and fall	Plot 10, fall
	0 to 1 foot depth									
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
1939:										
Apr. 1	16	21	17	16	27	44	12	11	12	10
May 6	17	16	16	12	19	22	15	16	16	15
June 2	50	40	20	15	17	20	22	35	35	17
July 5	42	26	16	15	19	35	15	25	24	11
Aug. 8	65	27	63	25	40	47	25	66	41	43
Sept. 9	45	74	47	36	36	32	21	50	40	60
Nov. 24	46	69	34	21	43	47	24	74	12	27
1940:										
Apr. 19	11	10	11	7	11	7	9	6	9	6
May 14	11	10	11	10	15	17	12	7	11	10
June 24	22	16	7	7	9	10	6	24	19	5
July 17	72	35	9	5	14	16	11	43	20	6
Aug. 6	35	27	14	3	10	11	6	6	9	15
1941:										
May 5	9	10	7	12	15	11	10	12	11	14
May 20	17	12	10	11	16	14	12	10	14	10
June 16	9	12	22	15	16	26	10	19	15	12
July 7	47	37	20	10	32	22	17	52	42	12
July 23	52	32	25	10	27	25	17	20	22	27
Aug. 20	35	29	20	14	38	27	12	46	27	47
Oct. 23	46	29	41	19	27	27	15	62	61	67
1942:										
June 3	24	11	7	16	12	26	12	16	11	17
July 7	29	24	21	30	29	19	15	14	19	26
	1 to 3 foot depth									
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
1939:										
Apr. 1	10	15	10	9	10	12	6	14	11	7
May 6	6	5	4	4	10	7	5	4	4	4
June 2	12	15	12	12	22	20	10	10	10	7
July 5	11	15	7	5	14	26	6	11	10	4
Aug. 8	4	7	14	6	10	9	6	6	10	12
Sept. 9	21	9	7	9	14	9	7	26	14	12
Nov. 24	30	9	9	6	9	9	11	15	14	7
1940:										
Apr. 19	5	5	4	5	5	4	4	6	3	3
May 14	5	4	5	3	4	5	3	1	4	3
June 24	6	4	6	3	6	3	4	3	4	3
July 17	7	3	5	3	4	4	4	4	5	1
Aug. 6	9	14	3	1	6	3	1	9	9	7
1941:										
May 5	5	3	4	4	4	5	1	3	9	4
May 20	6	6	4	5	6	4	1	6	1	3
June 16	5	6	5	7	7	4	5	5	6	4
July 7	7	7	10	3	15	5	10	7	7	7
July 23	17	27	7	5	7	7	10	15	12	5
Aug. 20	7	0	1	1	7	7	4	6	1	1
Oct. 23	6	9	6	4	10	5	14	9	9	26
1942:										
June 3	2	5	7	6	7	4	2	5	4	4
July 7	6	2	2	1	2	5	5	2	2	4

eral experience that the peach will respond to additions of nitrogen where prunes obtain an adequate supply.

Perhaps the most interesting data from this trial were obtained from the nitrogen analyses. These analyses were made on samples of leaves, twigs, and soil taken in the same manner as for peaches. The data are presented in tables 7, 8, and 9. The seasonal curves for soil nitrate (table 9) tend to follow the usual pattern of a spring minimum and a fall maximum as reported earlier by Proebsting (1933), modified in those plots receiving summer applications of ammonia. The check plots tend to be low throughout the period.

The twig samples (table 8) show the same tendency exhibited by the peach to reflect no increase in nitrogen until shortly before blossoming. In the prune material (as compared with the peach) there is less difference between fertilized and check trees, and the difference is less consistent. The increase noted just before blossoming in the peach in 1939 and in the prune in 1942 suggests translocation of nitrogen to the twigs before movement in the transpiration stream is possible.

The leaf samples reflect treatment fairly well (table 7). The check plots are lower than the fertilized plots in nearly all cases, and the differences tend to be at the maximum shortly after an application has been made.

SUMMARY AND CONCLUSIONS

Data are presented for a five-year period for peach and prune plots fertilized with nitrogen in the form of NH_3 and $(NH_4)_2SO_4$ at different seasons. Yield records and nitrogen analyses of soil and plant parts are included, together with some supplementary data. Peaches gave increased yields irrespective of time of application, with an indication that fall was a slightly less favorable season than spring or winter and that no advantage inheres in a split application. Prunes in the same soil type and district failed after five years to produce increased yields. Nitrogen applied as NH_3 in the irrigation water behaved essentially the same as $(NH_4)_2SO_4$. Nitrogen levels in the tissues analyzed reflected the treatments, and after an application they remained higher than in the check during the year until the next application. That is, at the rate used and for the conditions of the experiment, the time of applying nitrogen was a matter of minor importance.

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LITERATURE CITED

ALDRICH, W. W.
1931. Nitrogen intake and translocation in apple trees following fall, winter, and spring sodium nitrate applications. Amer. Soc. Hort. Sci. Proc. **28**:532–38.

BATJER, L. P., J. R. MAGNESS, and L. O. REGEIMBAL.
1943. Nitrogen intake of dormant apple trees at low temperature. Amer. Soc. Hort. Sci. Proc. **42**:69–73.

HENDRICKSON, A. H., and F. J. VEIHMEYER.
1942. Readily available soil moisture and sizes of fruits. Amer. Soc. Hort. Sci. Proc. **40**:13–18.

PROEBSTING, E. L.
1933. Effect of covercrops on the soil solution at different depths under orchard conditions. Hilgardia **7**:553–84.

PROEBSTING, E. L.
1937. Fertilizing deciduous fruit trees in California. California Agr. Exp. Sta. Bul. **610**:1–29.

PROEBSTING, E. L., and C. F. KINMAN.
1933. Orchard trials of nitrogen and phosphorus. Amer. Soc. Hort. Sci. Proc. **30**:426–30.

RUSSELL, E. J.
1932. Soil conditions and plant growth. 567 p. Longmans, Green, and Co., New York, N. Y.

COMPARATIVE BEHAVIOR OF AMMONIA AND AMMONIUM SALTS IN SOILS

H. JENNY, A. D. AYERS, AND J. S. HOSKING

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H. JENNY,[3] A. D. AYERS,[4] AND J. S. HOSKING[5]

INTRODUCTION

SOME YEARS ago anhydrous ammonia (NH_3) was introduced in California as a nitrogen fertilizer. This compound, sold as "Agricultural Ammonia" and "Shell NH_3," is available in the form of a liquefied gas compressed in strong steel cylinders that weigh about 150 pounds.

Agricultural Ammonia is applied on the land during irrigation. The cylinders are connected to a simple metering device, and the ammonia is released as a gas into the irrigation water. Thus the ammonia is distributed in a very dilute solution (100 to 500 p.p.m.). In water ammonia (NH_3) forms ammonium hydroxide (NH_4OH).

Every new method of fertilization unfolds problems for investigation. The mere fact that a new type of fertilizer initially produces good economic returns is no guarantee of lasting efficiency. Since the continued use of a given fertilizer may deteriorate the chemical and physical properties of a soil and impair the crop yields, it is, therefore, of utmost importance to acquire a clear understanding of the reactions that take place and the resulting changes in soil properties.

In this paper are discussed certain fundamental problems of ammonia fertilization, especially those phases that require laboratory investigation. For the purpose of comparison with commonly used nitrogenous fertilizers, all experiments with ammonia (NH_3) were accompanied by corresponding experiments with ammonium sulfate [$(NH_4)_2SO_4$] or ammonium chloride (NH_4Cl). The various topics investigated may be conveniently grouped as follows: (1) the extent and chemical nature of ammonia fixation in soils; (2) the availability of ammonia in soils to plants and microörganisms; (3) the influence of ammonia on physical soil characteristics, especially permeability.

FIXATION OF AMMONIUM COMPOUNDS IN SOILS

Experimental Procedure.—To 50-gram portions of air-dry soil were added electrolyte solutions containing 2 to 500 milliequivalents of NH_4OH or $(NH_4)_2SO_4$. All systems were brought to a volume of 1 liter. The suspensions were kept at room temperature for 24 hours and were shaken occasionally. Samples of clear supernatant liquid were obtained by centrifuging or by means of Pasteur-Chamberland filters. According to special tests, no NH_3 was lost under the experimental conditions. The NH_3 was determined by distillation with MgO into standard acid, using methyl red as an indicator.

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Influence of Soil Texture and Acidity.—Of the twenty-three soils investigated, three typical examples are shown in figure 1. Two features are outstanding: First, the total amount of nitrogen taken up varies with the kind of soil; second, the compounds NH_4OH and $(NH_4)_2SO_4$ behave differently in different soils. The Aiken clay loam, for example, fixes larger amounts of nitrogen from NH_4OH than from $(NH_4)_2SO_4$, whereas certain other soils,

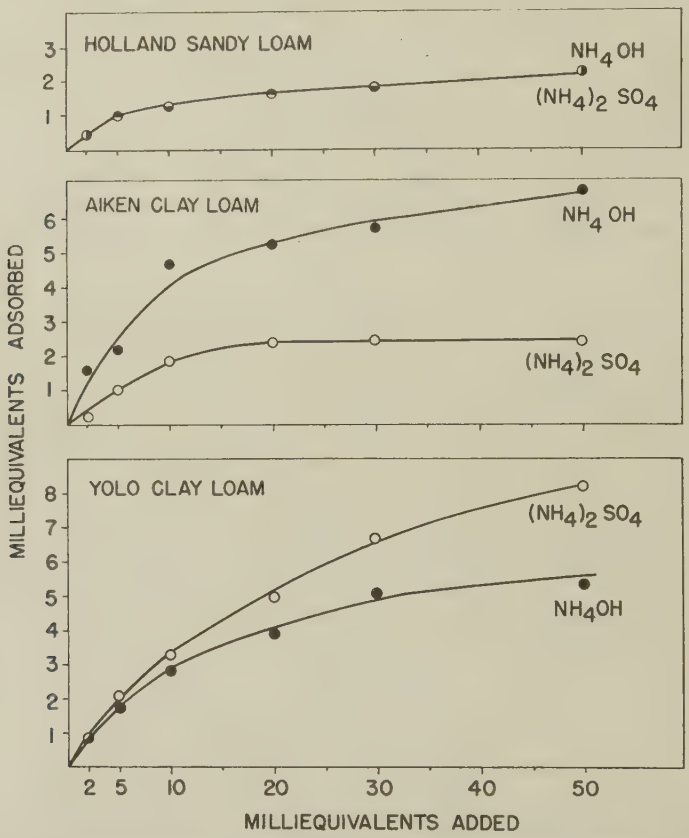


Fig. 1.—Typical examples of uptake of NH_4 from ammonium hydroxide and from ammonium sulfate by various soil suspensions. Note the variations in the relative position of NH_4OH and $(NH_4)_2SO_4$.

such as Yolo clay loam, fix larger amounts from $(NH_4)_2SO_4$. A few soils, for instance the Holland sandy loam, behave indifferently towards the two nitrogen compounds. These relations may well be examined in greater detail.

As has long been known, the adsorption of many electrolytes depends on the texture of the soil, particularly its colloid fraction. In this regard NH_4OH and $(NH_4)_2SO_4$ are no exceptions. This fact is clearly brought out in figure 2, which depicts the adsorption of nitrogen as a function of soil texture, the latter being expressed in terms of moisture equivalents. In general, the fine-textured soils exhibit higher nitrogen adsorption than the coarse-textured ones, from NH_4OH as well as from $(NH_4)_2SO_4$; but the correlation is far from

perfect. Judging from the distinct scattering of the data, other factors besides texture influence adsorption.

Inasmuch as solutions of NH_4OH are alkaline, whereas those of $(NH_4)_2SO_4$ are acid, there would probably be a correlation between the pH of the soil and NH_4 adsorption from the two solutions. This situation is well illustrated in

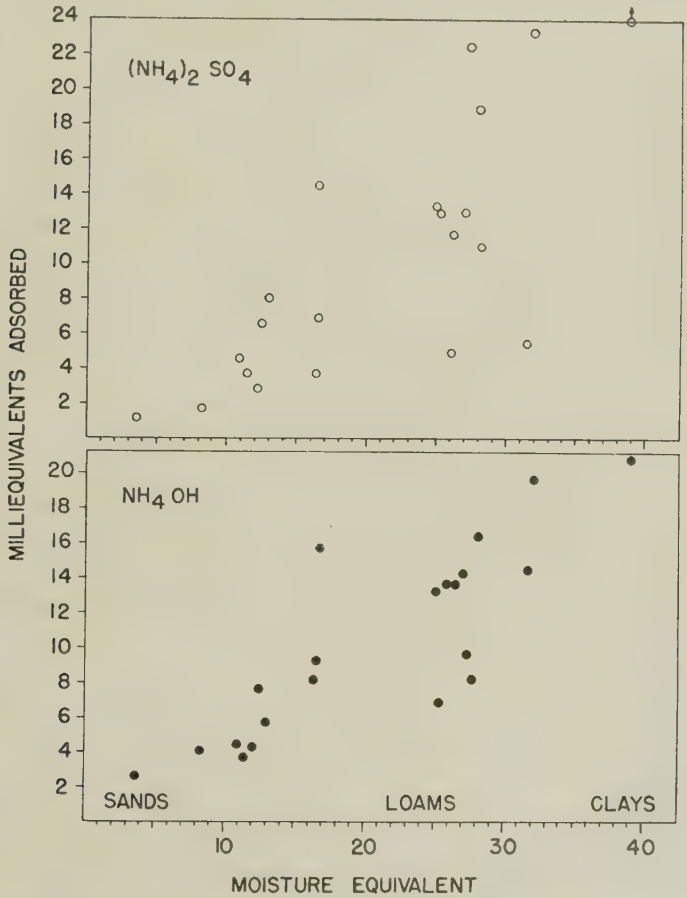


Fig. 2.—Relation between uptake of nitrogen and soil texture, the latter being expressed as moisture equivalents. Data refer to soil suspensions containing 50 grams of soil and 50 milliequivalents of nitrogen in a volume of 1 liter.

figure 3. On the abscissa is plotted the pH value of each soil;[6] and on the ordinate is indicated the difference between the NH_4 adsorption from $(NH_4)_2SO_4$ and the corresponding NH_4 adsorption from NH_4OH, at a NH_4 concentration of 50 milliequivalents in 1,000 cc of solution (compare fig. 1). As may be clearly seen, the relative NH_4 adsorption from the two electrolyte solutions depends upon the pH of the soil. Acid soils tend to adsorb more nitrogen from NH_4OH solutions, whereas alkaline soils favor $(NH_4)_2SO_4$.

[6] Soil-water ratio is 1:2; pH measured with a glass electrode.

Again wide differences exist among the soils of each group. Probably the crystalline nature of the colloidal material comes into play. The full significance of the nature of the clay colloids will become apparent later in this discussion.

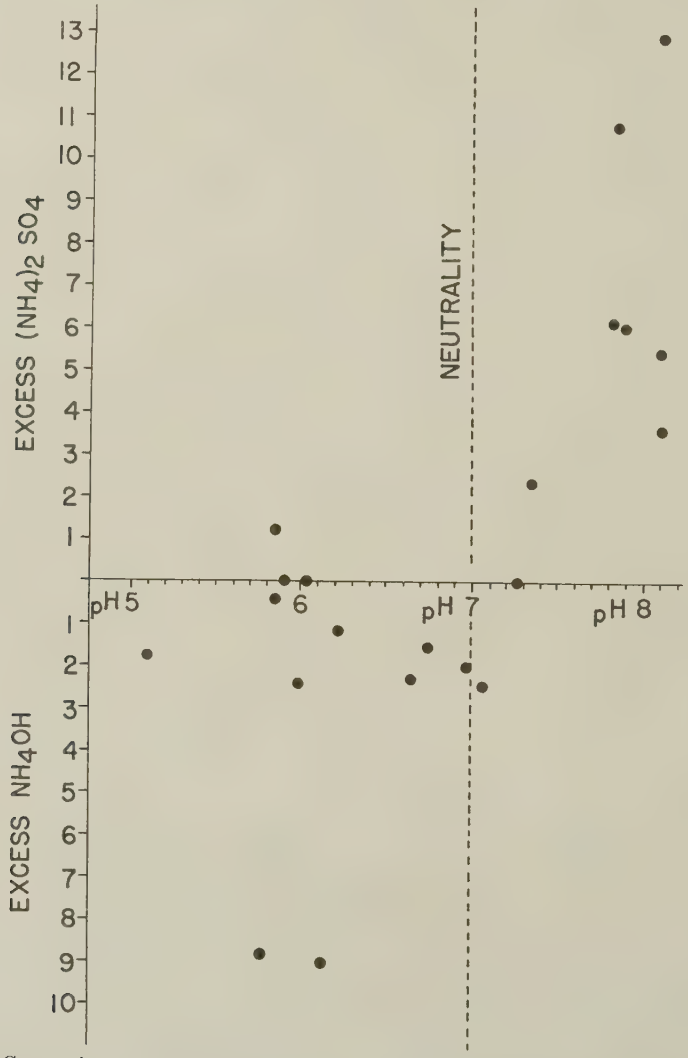


Fig. 3.—Comparison of nitrogen uptake from $(NH_4)_2SO_4$ and NH_4OH as related to the pH of the soil. On the abscissa are plotted the pH values of the various soils, on the ordinate the difference "nitrogen uptake from $(NH_4)_2SO_4$ minus nitrogen uptake from NH_4OH."

Effect of Soil-Water Ratio.—The data hitherto presented refer to systems composed of 50 grams of soil in 1,000 cc of solution. Under practical conditions of irrigation the proportion of soil to water differs from that of the systems mentioned previously. The amount of the solid phase exceeds that of the liquid phase. To ascertain how the ratio of soil to water affects NH_4 adsorption,

750 cc of a solution containing 6.67 milliequivalents of electrolyte per liter was added to each of a series of soil samples having different weights. Figures 4 and 5 show the results obtained for Aiken clay loam and Yolo clay loam. The percentage of nitrogen adsorbed is plotted as a function of cubic centimeters of solution per gram of soil. The electrolyte concentration of 6.67 milliequiv-

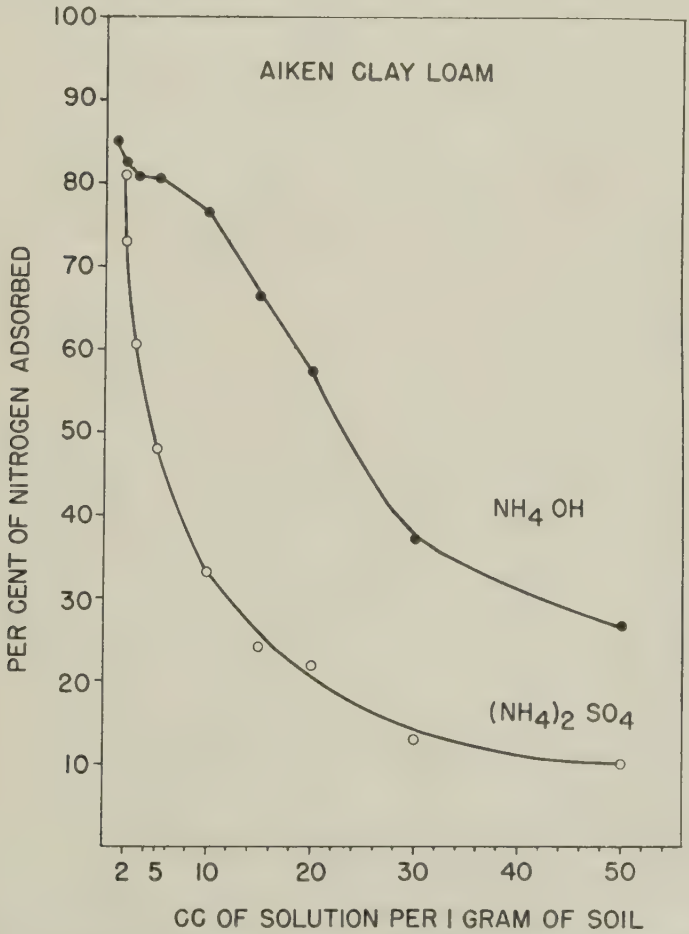


Fig. 4.—Percentage adsorption of NH_4 as conditioned by the soil-water ratio; 750 cc solution containing 6.67 milliequivalents of NH_4 in equilibrium with various amount of Aiken clay loam.

alents per liter is equal to 114 p.p.m. of NH_3, a value frequently used in irrigation practice.

Both figures 4 and 5 reveal a pronounced uptake of nitrogen at higher soil contents. Aiken clay loam maintains its preference for nitrogen from NH_4OH throughout the range of soil-water ratios investigated. With Yolo clay loam, the NH_4OH and $(NH_4)_2SO_4$ curves cross each other.

The soil-water ratios selected for these measurements pertain to systems

that range from suspensions to very thick muds. It is difficult if not impossible to measure NH_4 adsorption at such low moisture values as prevail under field conditions. Technical difficulties of extracting the soil solutions are greatly increased by such phenomena as hydration effects and perhaps Donnan equilibria.

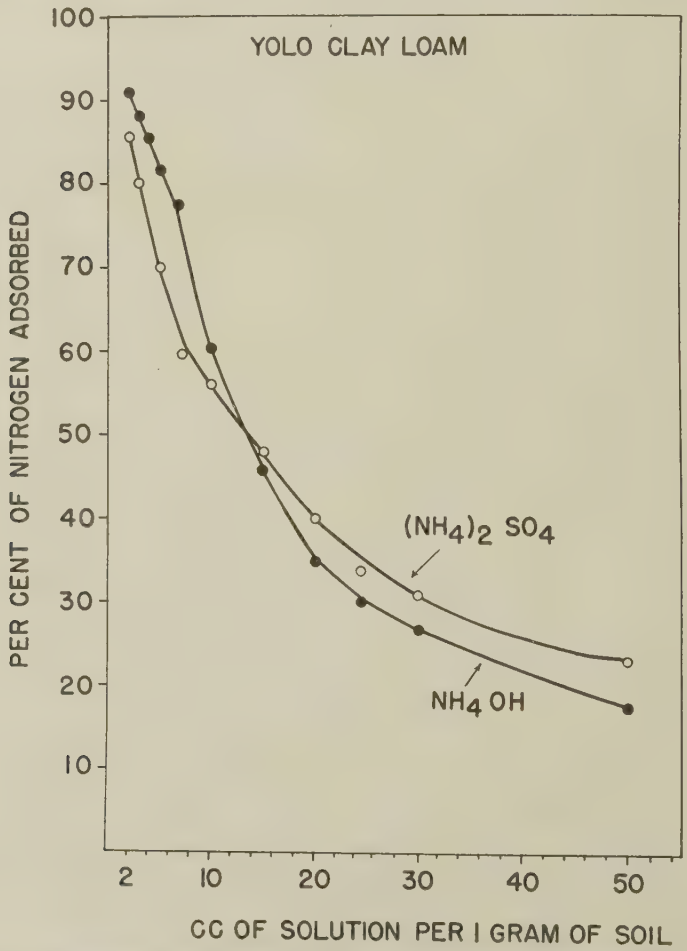


Fig. 5.—Percentage adsorption of NH_4 as conditioned by the soil-water ratio; 750 cc solution containing 6.67 milliequivalents of NH_4 in equilibrium with various amounts of Yolo clay loam.

To show the approximate intensity of nitrogen fixation at moisture percentages corresponding to field conditions, figure 6 was constructed. It is based on the fact (to be demonstrated in subsequent sections) that the adsorption of NH_4 ions involves a base-exchange reaction, which some investigators (*7, 9*)[7] have described quantitatively by an equation. With the assumption that the base exchange equation obtains throughout the moisture range under consideration, figure 6 plots the calculated fixation of NH_4 by a clay soil

[7] Italic numbers in parentheses refer to "Literature Cited" at the end of this paper.

having a base-exchange capacity of 30 milliequivalents per 100 grams and by a sandy soil with a capacity of 3 milliequivalents per 100 grams. On the abscissa are indicated the moisture percentages (on dry bases). By division by 100, these may be readily converted to the scales given in figures 4 and 5. The ordinate indicates the percentage of NH_4 adsorbed from 6.67 milliequivalents of $(NH_4)_2SO_4$. The curve calculated for the clay soil agrees well with the

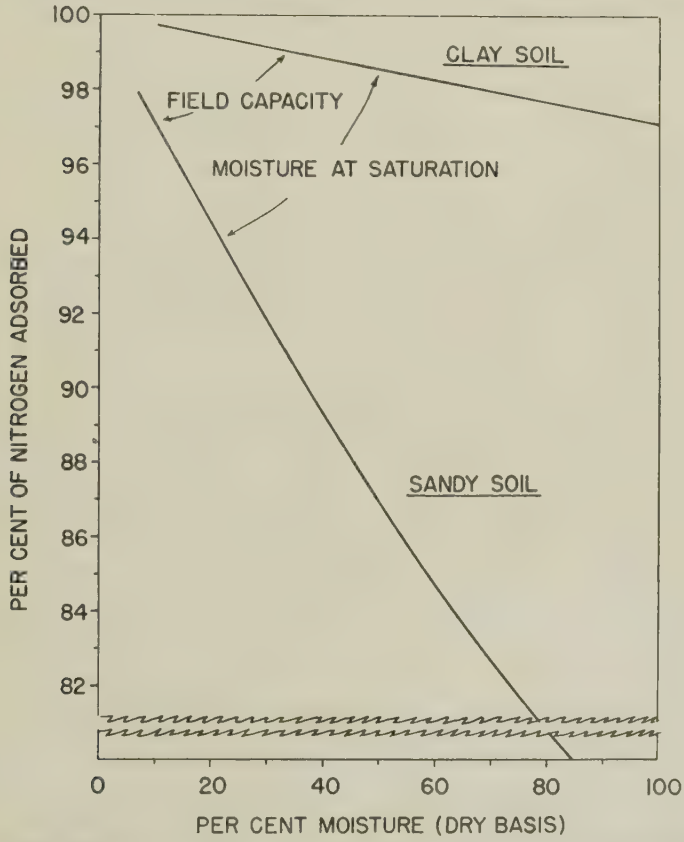


Fig. 6.—Extension of soil-water relations shown in figure 5 to field conditions (small values of soil-water ratios).

extrapolated curve of figure 5. The curve for the sandy soil is considerably below that of the clay soil, a feature in harmony with the adsorption data presented in figure 1. The graph also lists the approximate moisture percentages for the field capacity and for the soil system saturated with water. The latter corresponds to the water conditions during irrigation; the former reflects the approximate degree of moisture a few days thereafter.

From the experimental as well as the theoretical evidence, one may safely conclude that under field conditions the percentage fixation of NH_4 assumes very high magnitudes.

Distribution of NH_4 in Relation to Depth.—Many farmers firmly believe that NH_3 dissolved in irrigation water distributes itself in the soil in ac-

cordance with the depth of penetration of water. Although such behavior is characteristic of nitrates (NO_3), it need not occur with NH_3 and with NH_4 compounds.

To obtain a quantitative estimate of the distribution of ammonium fertilizers in relation to depth, brass cylinders 1 inch in diameter and 6 to 8 inches in length were filled with various types of soils (400 grams). The brass cylinders consisted of sections of short cylinders, each 1 inch long—an arrange-

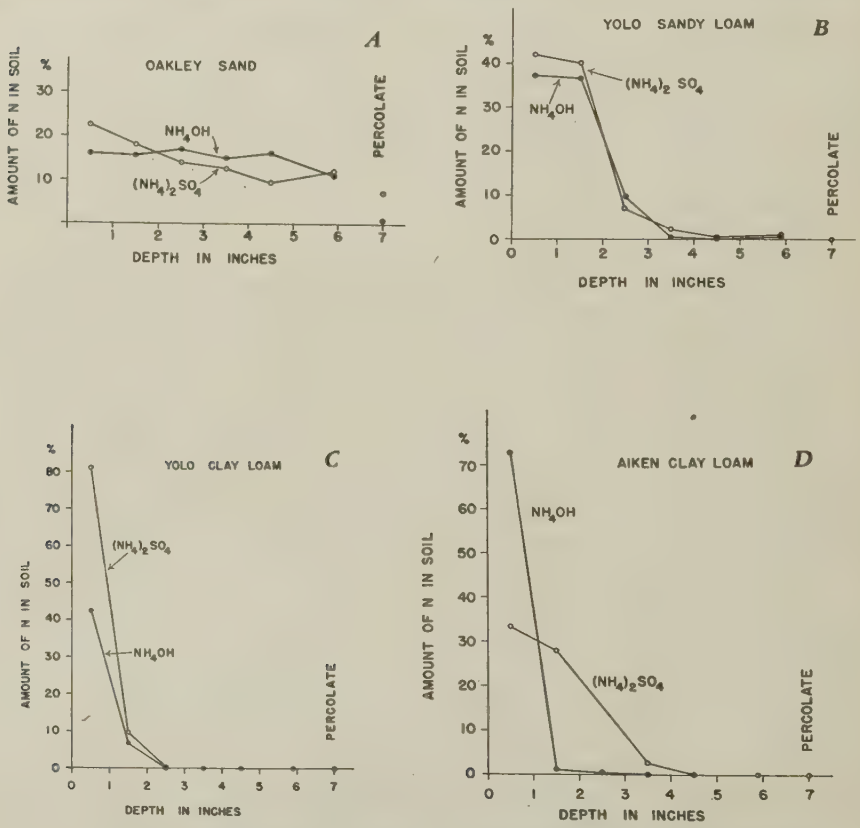


Fig. 7.—Amount of nitrogen found in soil sections in percentage of nitrogen added.

ment that permitted the entire soil column to be sliced into 1-inch segments whenever desired. Through these columns was passed 500 cc of NH_4OH or $(NH_4)_2SO_4$ solution containing 7.5 milliequivalents of nitrogen (127 p.p.m. NH_3). This volume corresponds to an irrigation of 10 acre-inches. After the experiment the column was taken apart, and the 1-inch segments were analyzed individually.

The soils investigated included textures from sandy to clay. The following twelve types were examined: Oakley sand, Goldridge fine sandy loam, Hanford fine sandy loam, Fresno fine sandy loam, Yolo sandy loam, Vina silt loam, Yolo silt loam, Ramona loam, Yolo clay loam, Aiken clay loam, Aiken clay, and Altamont adobe clay.

The results are summarized in the characteristic patterns given by figure 7. Nitrogen penetration is evidently deep in light soils and shallow in heavy ones. In sands (fig. 7, *A*), nitrogen distributes itself rather evenly throughout the 7-inch column; and, furthermore, the percolating solution contains appreciable nitrogen. In medium-textured soils, as illustrated by Yolo sandy loam (fig. 7, *B*), the bulk of the nitrogen, in the form of NH_4OH or $(NH_4)_2SO_4$, is held in the first 3 inches of soil. The percolating solution is almost free of nitrogen. This behavior is especially characteristic of heavy-textured soils such as Yolo clay loam (fig. 7, *C*), in which nitrogen penetration is restricted to the first 2 inches. The lower portions of the column receive no measurable amounts of nitrogen. These observations agree with the previously mentioned studies which demonstrated that the fixation of NH_4 is directly related to the colloid content of the soil.

The Aiken series, which has an acid reaction and contains kaolinitic rather than montmorillonitic clay particles, deviates from the behavior of the neutral Yolo soils in one important respect. NH_4OH and $(NH_4)_2SO_4$ penetrate at widely different rates. The major fraction of the NH_4OH is held in the surface inch of soil, whereas in the columns receiving $(NH_4)_2SO_4$, the second inch contains nearly as much nitrogen as the first. Moreover, $(NH_4)_2SO_4$ percolates much deeper in Aiken clay loam than in any other soil of similar colloid content. These findings harmonize with figure 3, which emphasizes the role played by soil acidity and, perhaps, by the crystalline nature of the clay minerals.

The question arose whether subsequent leachings with distilled water would release the adsorbed NH_4 and carry it deeper. To examine this possibility, ammoniated soils were prepared by leaching 1-inch soil columns (Yolo clay loam and Aiken clay loam) with 250 cc of NH_4OH or $(NH_4)_2SO_4$ containing 12 milliequivalents of nitrogen per liter. For either electrolyte, over 98 per cent of the nitrogen applied was held by these 1-inch columns. The only exception was Aiken clay loam, which retained only 62.6 per cent of the NH_4 applied as $(NH_4)_2SO_4$.

Immediately after percolation had ceased, 250 cc of distilled water was passed through the column, and the new percolate was analyzed for nitrogen. Since in Yolo clay loam only about 6 per cent of the nitrogen was removed by this treatment, evidently the adsorbed NH_4 ions were rather tightly held. The leachates of Aiken clay loam contained even less nitrogen—1.6 per cent only.

In medium- and fine-textured soils, then, NH_4 apparently does not follow the movement of the irrigation water, but accumulates in a relatively shallow surface zone. After a time, fortunately, nitrification takes place; and part of the adsorbed nitrogen is converted to NO_3, which may be carried readily into deeper horizons.

Often the irrigation water contains dissolved salts, which theoretically might hinder the adsorption of NH_4 by way of cation competition. Tests conducted with $(NH_4)_2SO_4$ and NH_4OH in presence of $CaCl_2$ and $NaHCO_3$ (5 to 15 milliequivalents per liter of solution) did not, however, reveal any significant effect on the distribution of NH_4 in the soil columns.

MECHANISM OF FIXATION OF AMMONIUM COMPOUNDS

Because of the close correlation between soil texture and the adsorption of cations from electrolyte solutions, soil chemists have intensively investigated the base-exchange properties of the colloidal fraction of the soil. They have shown repeatedly that the colloidal clay and humus particles govern the fixation processes of ammonium ions. It will prove advantageous to discuss separately the behavior of NH_4OH and that of its salts, the sulfates and the chlorides.

BEHAVIOR OF AMMONIUM SALTS

Since the days of Thomas Way (1850) chemists have known that the fixation process of $(NH_4)_2SO_4$ and NH_4Cl involves the cation (NH_4) only. The anion does not participate. The mechanism involves an exchange process. For a given amount of NH_4 taken up, an equivalent amount of other cations is released by the colloidal particle. A typical reaction may be formulated as follows:

$$\boxed{\text{Clay}}\ K + NH_4Cl \rightleftharpoons \boxed{\text{Clay}}\ NH_4 + KCl$$

The extent of the reaction (from left to right) depends on numerous factors such as salt concentration, clay-water ratio, and temperature. Quantitative descriptions have been formulated by various investigators (*7, 9*).

For illustration we may present the data obtained with Yolo colloid and Aiken soil. The colloidal fraction ($<2\mu$) of Yolo clay loam and the samples

TABLE 1

CATION EXCHANGE BETWEEN K SYSTEMS AND AMMONIUM COMPOUNDS
(Total volume of systems = 500 cc)

Nature of system and amount of clay or soil used	Exchangeable K	Hydrolysis	Electrolyte added		NH_4 adsorbed	K released
	m.e.	*m.e.*		*m.e.*	*m.e.*	*m.e.*
K-Yolo clay,* grams:						
8.29	4.50	0.41	NH_4Cl	4.50	2.07	1.89
8.29	4.50	0.41	NH_4OH	4.50	1.75	0.68
K-Aiken soil,* grams:						
5.11	5.11	1.07	$(NH_4)_2SO_4$	5.11	1.84	1.99
5.11	5.11	1.07	NH_4OH	5.11	1.69	0.61
K-Aiken soil,† grams:						
25.00	5.18	1.35	$(NH_4)_2SO_4$	5.18	1.66	1.81
25.00	5.18	1.35	NH_4OH	5.18	2.12	0.62

* Prepared by leaching with KCl.
† Prepared by leaching with potassium acetate.

of Aiken clay loam were transformed into K systems—that is, systems containing only exchangeable potassium ions. These K-clays hydrolyze to the extent shown in table 1. After the addition of NH_4Cl or $(NH_4)_2SO_4$ or NH_4OH, the reaction was allowed to proceed for several days at constant temperature. The solid particles were then separated by ultrafiltration or centrifugation, and potassium and NH_4 were determined in the ultrafiltrate or in the super-

natant liquid. Table 1 gives the amounts of NH_4 taken up and of potassium released (corrected for hydrolysis).

Focusing attention on NH_4Cl and $(NH_4)_2SO_4$, we see that the exchange is practically stoichiometric. For every NH_4 ion taken up, a potassium ion has been released from the clay particles. This holds true both for the Yolo colloid and for the Aiken soil.

Calcium clays behave likewise. In an experiment by W. P. Kelley,[8] 10 grams of Yolo soil possessing 2.94 milliequivalents of exchangeable calcium ions (but

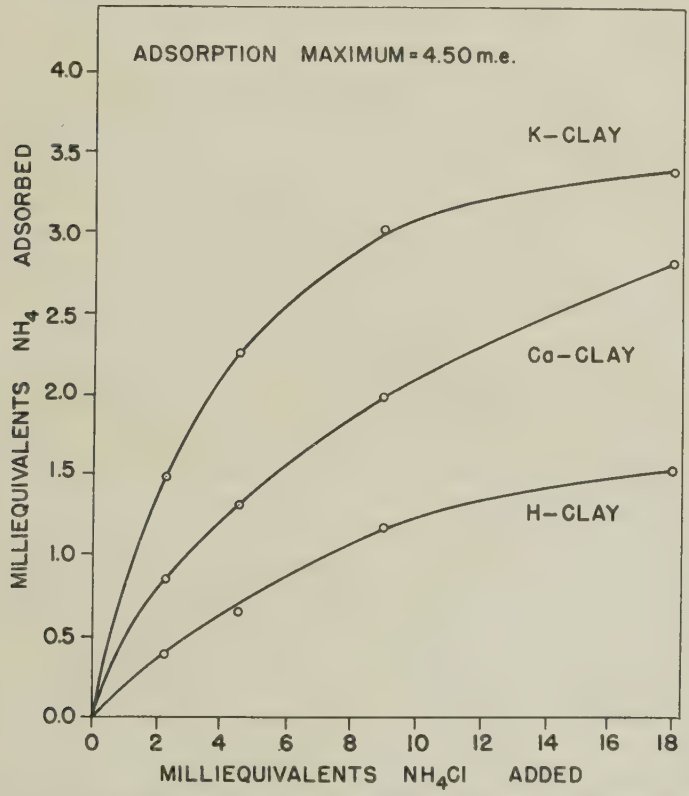


Fig. 8.—Amounts of NH_4 adsorption from NH_4Cl in three clay systems. The fixation of NH_4 depends on the nature of the cation on the colloidal clay.

no other exchangeable cations) reacted with 2.94 milliequivalents of NH_4Cl in 100 cc volume. The NH_4 adsorbed amounted to 0.97 milliequivalent; the calcium released to 1.01. Again the exchange took place in stoichiometric proportions. For every divalent calcium ion released, two monovalent NH_4 ions were taken up by the soil.

As will be noted, the percentage adsorption of NH_4 is higher in the K system than in the Ca system—namely, 46 per cent as compared with 33. In other words, NH_4 fixation depends on the nature of the exchangeable ion on

[8] Kelley, W. P. Personal communications.

the clay. Figure 8 well illustrates this fact. It refers to pure K-clay, Ca-clay, and H-clay systems (500 cc), each containing 7.5 grams of clay (montmorillonite type) and 4.50 milliequivalents of exchangeable cations. H-clay, which corresponds to an acid soil, fixes the smallest amount of NH_4 ion from NH_4Cl as well as from $(NH_4)_2SO_4$. In the farming regions of California, where soil leaching is not pronounced, the curve depicting the reaction with Ca-clay may be taken as the most appropriate example.

Importance of the Degree of Saturation, with Special Reference to Potassium.—From the viewpoint of fertilizer practice, it is interesting to examine more closely certain aspects of the liberation of adsorbed cations such as potassium by additions of ammonium fertilizers.

As shown in figure 8, NH_4 salts added to a pure K-clay release considerable potassium. The liberation may be materially reduced if, besides potassium, other cations also are present on the clay particles. The proportion of exchangeable potassium in relation to the other exchangeable cations is known as the degree of saturation of potassium. It is usually expressed on a percentage basis. Thus if a given soil contains 20 milliequivalents of exchangeable cations, and if 5 milliequivalents of these are potassium, then the degree of saturation of potassium is $\frac{5}{20} \times 100 = 25$ per cent. The remaining 75 per cent of cations may be designated as complementary exchangeable ions.

To understand fully how the degree of saturation will affect plant nutrition and fertilizer applications, we must consider two separate aspects. These will be clearer if we restrict the discussion to hypothetical examples, assuming that all ions participating in the exchange have equal adsorption energies—that is, are held to the surface of the clay particles with equal forces.

Case I: Release of potassium when NH_4Cl is added in proportion to the base-exchange capacity of the soil. Suppose we consider the release of potassium upon addition of NH_4Cl in amounts equal to the base-exchange capacity. Calculations indicate that under such conditions the replacement of potassium is always 50 per cent of the amount of potassium on the clay, no matter what the degree of saturation. This relation is illustrated in figure 9 by a straight line parallel to the horizontal axis.

Case II: Release of potassium when NH_4Cl is added in proportion to the amount of exchangeable potassium in the soil. Suppose we select the specific case in which the amount of NH_4Cl is equal to the amount of exchangeable potassium. According to calculations as well as experiments, under these conditions the replacement of potassium strongly declines as the degree of saturation becomes less (curve II in fig. 9). In most soils the degree of saturation of potassium is very low—considerably under 10 per cent. In consequence, the liberation of adsorbed potassium upon addition of NH_4 fertilizers is apt to be of a small magnitude.

BEHAVIOR OF AMMONIA (NH_4OH, NH_3)

Unlike NH_4Cl and $(NH_4)_2SO_4$, which are strong electrolytes, NH_4OH is a weak base. An aqueous solution of ammonia contains NH_4 ions as well as NH_3 molecules. Since, moreover, the anion is OH, additional complications are introduced in the adsorption mechanism.

According to the exchange experiments reported in table 1, the amount of potassium released by NH_4OH is much smaller than in the corresponding studies with NH_4Cl or $(NH_4)_2SO_4$. Presumably the small exchange of potassium is due to the limited number of NH_4 ions in the hydroxide solution. In contrast to the NH_4 salt solutions, the amount of nitrogen taken up from NH_4OH greatly exceeds the amount of potassium replaced. The excess of nitrogen adsorbed over potassium released presumably results from NH_3 ad-

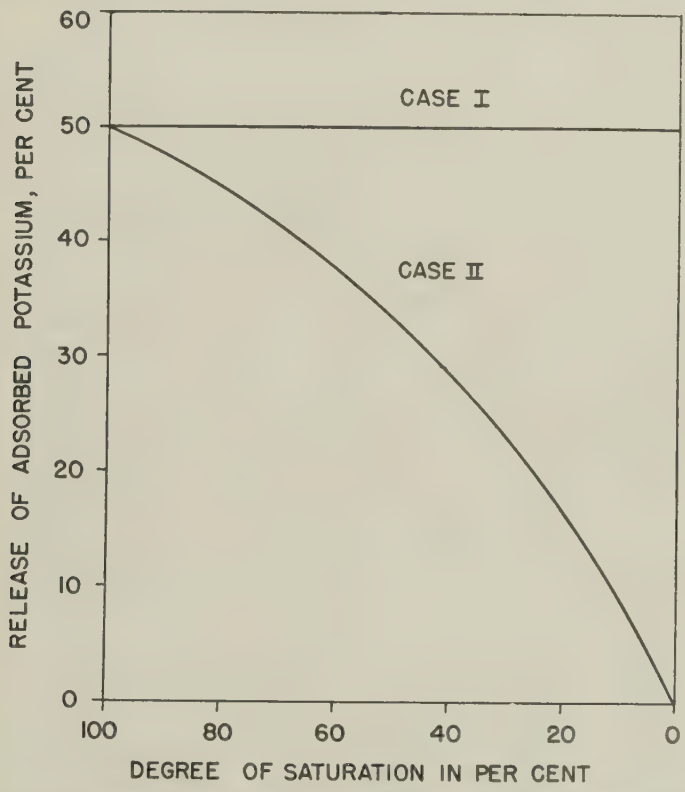


Fig. 9.—Release of adsorbed potassium by ammonium compounds as influenced by the degree of saturation of potassium.

sorption and from the reaction of NH_4OH with hydrogen ions of the clay. These two processes were studied with the aid of titration curves and by exposing clays to NH_3 vapor.

Titration Curves.—Colloidal clays extracted from soils of the Yolo and the Aiken series were converted into H-clays by electrodialysis. Suspensions containing 1 gram of clay in 100 cc of solution gave a pH reading (glass electrode) of 4.30 for Yolo colloid and 6.67 for Aiken colloid. To these acid systems were slowly added increasing amounts of NH_4OH. The pH values obtained as a function of NH_4OH added are illustrated by the titration curves of figure 10. In comparison with distilled water and washed quartz sand, the clay sys-

tems are strongly buffered against NH_4OH—a feature very pronounced in the Yolo colloid. The reaction taking place may be formulated as follows:

Judging from the shape and position of the curves, H-Aiken colloid acts as a much weaker acidoid than H-Yolo colloid.

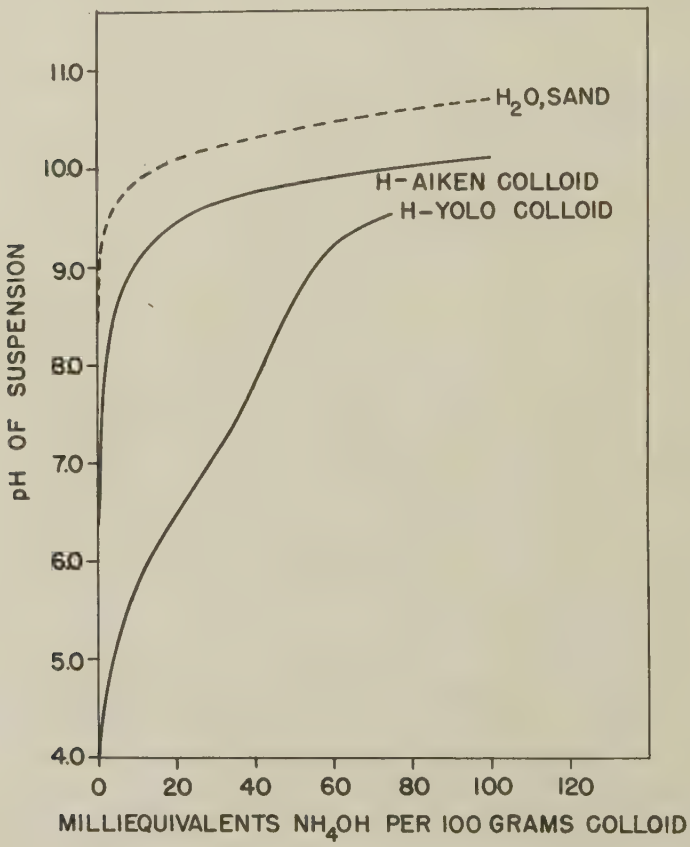


Fig. 10.—Titration curves of electrodialyzed colloidal clays with NH_4OH (1 per cent suspensions).

Under conditions of soil formation in California the colloids of the Yolo type are completely saturated with bases, and those of the Aiken type are nearly so. Naturally, therefore, the titration curves of the natural soils will differ markedly from those of their electrodialyzed colloids. As figure 11 shows, the addition of small amounts of NH_4OH to 5 per cent suspensions of natural soils increases the soil alkalinity to values exceeding pH = 10. In many soils (for example, Ramona and Yolo) the pH resulting from addition of NH_4OH is higher than the pH value obtained by adding NH_4OH to corresponding amounts of distilled water. This increase in pH may be explained

by the release of exchangeable calcium ions by NH_4 ions, resulting in the formation of $Ca(OH)_2$, a stronger base than NH_4OH.

The increase of alkalinity upon the addition of NH_4OH may temporarily upset the physiological balance of the plants growing in the soil. In most soils, however, NH_4 is readily nitrified, so that the reaction is shifted toward the neutral point.

Fixation of NH_4 as a Function of the pH of the Solution.—As may be seen in figure 11, the Aiken clay is strongly buffered at high pH values. Con-

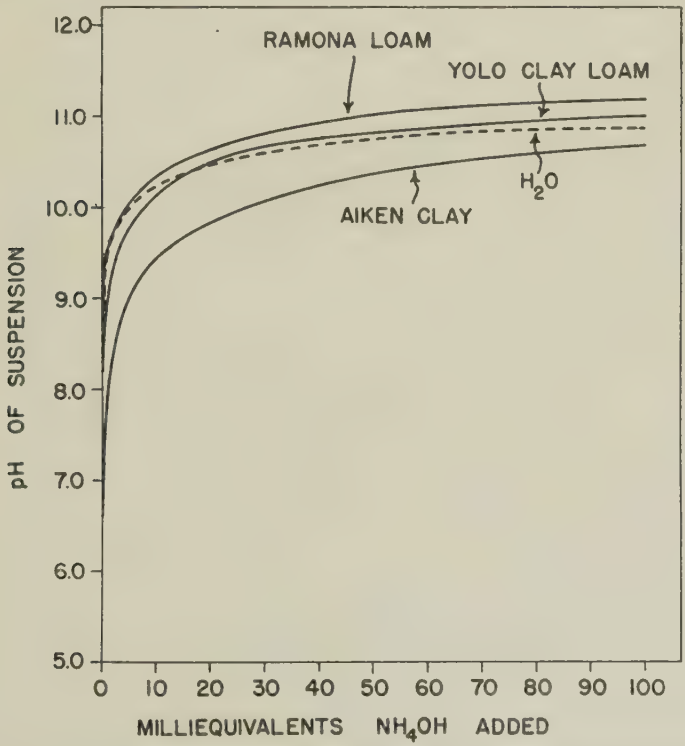


Fig. 11.—Titration curves of natural soils with NH_4OH; milliequivalents per 100 grams of soil.

ceivably, then, the OH ions of the crystal lattice of the kaolinitic clays of the Aiken soils may participate in the reaction. To test this possibility, the base-exchange capacity of Aiken colloid and Yolo colloid for NH_4 was ascertained as a function of pH. Solutions of varying pH were prepared by adding NH_4OH or acetic acid to normal ammonium acetate. From 1 to 2 grams of the colloidal material was mixed with 100 cc of ammonium acetate solution. When the mixture had been digested on the water bath for 2 hours at 65° C, the samples were transferred to a Büchner funnel and leached with 1,000 cc of the same solution. After suction had been applied, the excess ammonium acetate was removed by leaching the clays with 50 cc of methyl alcohol. Dilute HCl was immediately added to the sample in order to prevent losses of NH_3

by evaporation. The amount of nitrogen fixed by the clay was determined by distillation.

In figure 12 appear the results for various colloids and soils. The striking difference between kaolinitic and montmorillonitic (bentonitic) material is noteworthy. Clays of the montmorillonite type such as bentonite and Yolo colloid adsorb nearly constant amounts of NH_4, irrespective of the pH of

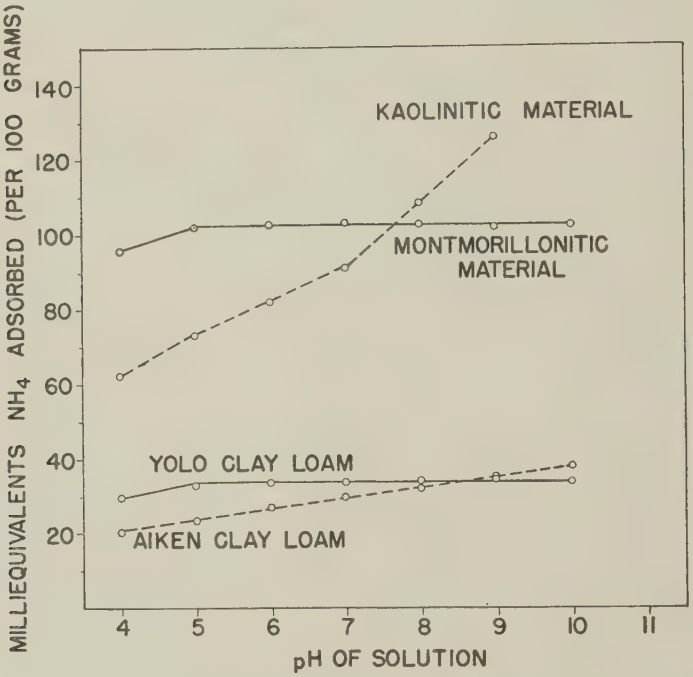
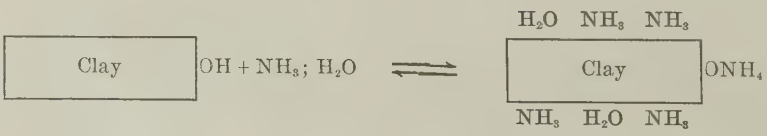


Fig. 12.—Adsorption capacity of various colloidal clays and soils for NH_4 as conditioned by the pH of the solution.

the solution. On the other hand, the kaolinitic materials such as kaolinite, halloysite, and Aiken clay fix much more nitrogen at high than at low pH values. This behavior is undoubtedly associated with the crystalline structure of the materials. Unlike the montmorillonitic, the kaolinitic clays contain sheets of OH ions as an essential part of the crystal lattice. With increasing pH, evidently, the exposed OH groups react progressively with the NH_4 ions of the solution; hence the adsorption capacity varies as a function of pH (*5*).

The question of the adsorption of NH_3 molecules was investigated by exposing dry H-clay to vapors containing variable proportions of NH_3 and H_2O molecules. The reactions to be expected may be shown by the following scheme:



Under the experimental conditions one would expect a molecular adsorption of NH_3 as well as a chemical reaction of NH_3 on the exposed OH ions of the clay lattice (*4*).[9]

The H-Yolo clays used have a base-exchange capacity of 64 milliequivalents per 100 grams as determined by the ammonium acetate method. Leaching of H Yolo with KCl and titration of the filtrate with NaOH give a capacity of 60 milliequivalents per 100 grams. H-Yolo clay samples were dried in the oven at 80° C and then placed in desiccators that contained NH_4OH solutions of various concentrations. After one week the samples were removed, and the

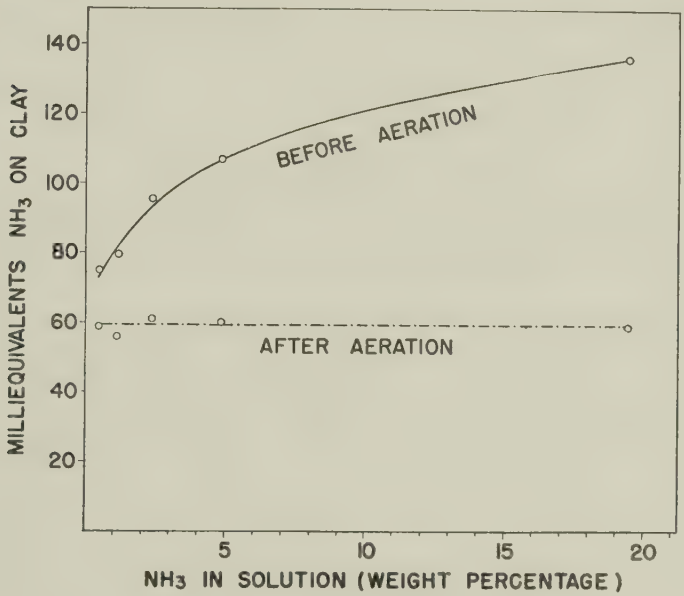


Fig. 13.—Adsorption of NH_3 gas by H clay.

total nitrogen adsorbed was determined by distillation. The results are portrayed in figure 13 by the solid curve, which has the characteristics of an adsorption isotherm. In a parallel experiment the samples, after removal from the desiccators containing ammonia solutions, were transferred to aerators; and a current of dry, filtered air was passed through the apparatus for 4 days. Subsequently, the NH_3 remaining on the clay was determined by distillation. According to the dashed curve in figure 13, the nitrogen content of the aerated clay samples is independent of the NH_3 concentration in the vapor phase. The amount of NH_3 fixed corresponds closely, moreover, to the saturation capacity of the clay particles. Evidently we are dealing here with the reaction

$$\boxed{\text{Clay}}\,OH + NH_3 \rightleftharpoons \boxed{\text{Clay}}\,ONH_4$$

The difference between the two curves in figure 13 is probably a measure of

[9] These aspects have since been studied in considerable detail in the University of California Division of Soils laboratory.

the NH_3 molecules held loosely on the surface of the clay particles. These molecules may be readily removed by a current of air, whereas the NH_3 molecules combined with the hydrogen ions of the lattice adhere much more tightly to the surface. According to computations involving a comparison between the proportions of NH_3 and H_2O molecules in the vapor phase and on the clay particles, the NH_3 molecules at low partial pressures of ammonia have little chance to remain on the clay surface, because of competition with H_2O molecules. This probably explains why, in dilute clay suspensions, NH_3 molecules are not adsorbed by the clay in large amounts.

According to these experiments, NH_3 gas could be utilized for fertilizing soils in nonirrigated areas. A tank of NH_3 could be placed on a plow or disk, and the gas could be led through a nozzle into the soil, several inches below the surface.[10] Fixation would immediately take place in accordance with the chemical equation given on page 444.

BIOLOGICAL EXPERIMENTS

Although the relation of nitrogen fertilization to crop yields is beyond the scope of this investigation, certain aspects pertaining to availability of adsorbed NH_4 and its nitrification by microörganisms lend themselves to laboratory tests.

Availability of Adsorbed NH_4 to Plants.—All data presented in this study indicate that nitrogen, in the form of $(NH_4)_2SO_4$ or NH_4OH, is held in the soil primarily as an NH_4 ion. In contrast to nitrate nitrogen, which is a mobile constituent of the soil solution, NH_4 is largely immobilized. Although plants readily adsorb nitrates from solution, there are no reliable data on the availability of NH_4 that is adsorbed on clay particles.

This problem was examined by adapting the culture-solution method of Hoagland and Broyer (*6*) to the requirements of colloidal-clay research. Barley plants 3 weeks old were decapitated, and the roots were placed in flasks containing the test solution. After 10 hours the roots were removed, washed, dried, and analyzed. According to Hoagland and Broyer, freshly excised barley roots are in an active state of metabolism and adsorb nutrients as readily as roots not severed from the shoots.

In each flask 100 grams (fresh weight) of excised roots were immersed in 3 liters of test solution. Two corresponding series of test solutions were used—the first a series of $(NH_4)_2SO_4$ solutions, and the second a series of clay suspensions that contained NH_4 in the adsorbed form. The total nitrogen in the media varied from 0.75 to 27 milliequivalents. Besides varying amounts of NH_4, all solutions contained a constant amount (3 milliequivalents) of potassium, either as K_2SO_4 or as K-clay.

Figure 14 shows graphically the intake of NH_4, as computed from total nitrogen determinations of the roots before and after experimentation. The higher the amount of NH_4 in the nutrient medium, the more nitrogen the roots absorb. The differences between the two curves are probably not significant and are accounted for by root variability and experimental errors. There exists little doubt that in this experiment the roots accumulate nitrogen with equal ease from NH_4Cl and NH_4-clay.

[10] A patent has since been obtained for this process (F. H. Leavitt, No. 2,285,932).

Throughout the experiment the roots also absorbed potassium. This intake was greatest at low concentrations of NH_4 and decreased as the amount of NH_4 in the solution and suspensions increased. In these experiments, therefore, large amounts of NH_4 tended to repress the accumulation of potassium by the roots. Probably the degree of saturation or complementary-ion principle outlined on page 440 was operating.

Studies on Nitrification.—Under normal field conditions NH_4 compounds in the soil are changed to nitrates by the activities of microörganisms. To

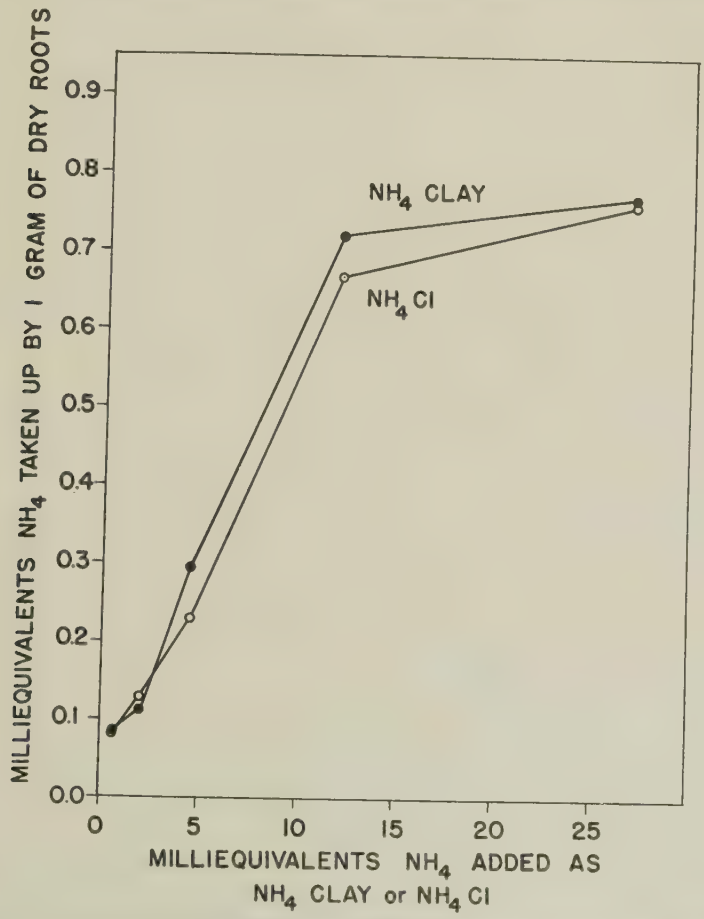


Fig. 14.—Uptake of NH_4 from NH_4-clay and NH_4Cl by excised plant roots. This graph demonstrates a high degree of availability of adsorbed NH_4.

obtain some information regarding the speed of nitrification and the individual behavior of NH_4OH and $(NH_4)_2SO_4$ during the process, laboratory experiments were conducted with Aiken clay loam and Yolo clay loam. The soils were ground and sieved (1-mm mesh), and 100-gram portions were placed in glass tumblers. Each soil was subjected to three series of treatments. To each sample was added, in the first series, 25 cc of distilled water; in the

second series, 25 cc of NH_4OH solution containing 5 mg of nitrogen; in the third series, 25 cc of $(NH_4)_2SO_4$ solution containing 5 mg of nitrogen.

The transformation of NH_4 into nitrate was measured weekly by the phenoldisulphonic acid method. The data plotted in figure 15 show the amounts of nitrate—expressed as nitrogen—that were found in the treated soils in excess of the amounts in the checks (soils receiving distilled water). Under the experimental conditions, 3 to 4 weeks were required to convert half the ammonia nitrogen into nitrate nitrogen. In the field, oxidation may proceed

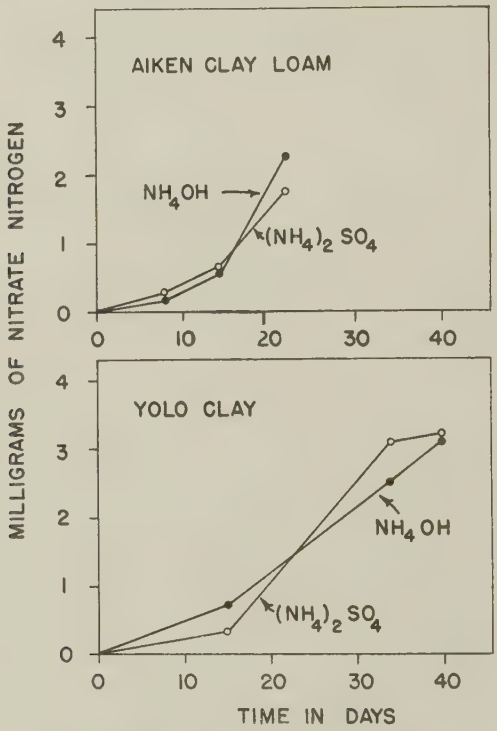


Fig. 15.—Nitrification of NH_4OH and $(NH_4)_2SO_4$ added to Yolo clay and Aiken clay loam. The curves show the nitrate nitrogen in the treated soil in excess of the checks.

faster or slower than in this example, depending on moisture, aeration, temperature, and other conditions. No significant difference, apparently, exists between the behaviors of NH_4OH and $(NH_4)_2SO_4$ at the low concentration employed.

Nitrification was also studied with NH_4 in the adsorbed state. An artificial soil was made up by mixing silica sand and Yolo clay containing adsorbed ammonium, potassium, calcium, and magnesium ions. To 50 grams of this material a small amount (0.5 gram) of fresh garden soil was added in order to provide the necessary microbiological population. The results resembled those shown in figure 15, except that the rate of nitrification was somewhat smaller at the beginning of the experiment than that observed with the natural soils. Evidently, adsorbed NH_4 may be readily oxidized to nitrates (*1*).

INFLUENCE OF NH_4 COMPOUNDS ON WATER PENETRATION

In irrigation agriculture, the rate at which water penetrates the soil is important. Accurate information on the effect of ammoniated irrigation water on soil permeability would therefore be interesting and significant. Such a study is also pertinent in view of the many contradictory claims advanced regarding the specific influence of NH_3 on water penetration.

Description of Method.—Soil samples were crushed, passed through a 1-mm sieve, and packed in metal tubes 2 inches in diameter and 8 inches in length. Successive 100-gram portions were placed in the tubes and subjected to ten

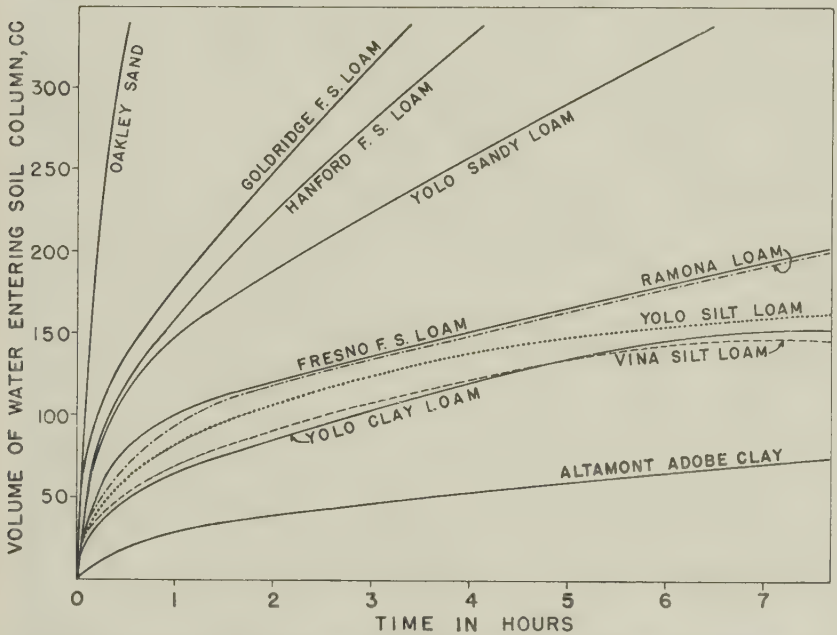


Fig. 16.—Entry of distilled water into soil columns, as influenced by soil type.

compacts with a standard compactor instrument. About four 100-gram portions were necessary to fill each tube. Metal screens placed at the bottom and top of the soil column provided support and stability and reduced possible disturbances of the surface of the soil. A 2-cm head of solution above the surface was maintained throughout the experiment. The volume of solution entering the soil column (infiltration) was calculated from the amount of liquid necessary to maintain constant head. The solution leaving the bottom of the column (percolation) was also measured frequently. All experiments were run in triplicate or quadruplicate in a room of nearly constant temperature. Over a dozen soils, comprising a wide variety of textures, were investigated.

Infiltration and Percolation of Distilled Water.—Curves in figure 16 depict the entry of distilled water into dry soil columns. The vertical axis indicates, in cc, the accumulative amount of water that has entered the soil column during a given period. The time is plotted on the horizontal axis. The

dominating influence of texture on water infiltration is an impressive feature of the graph. The time required for the dry soil column to take up 100 cc of water is 3 minutes for Oakley sand, 150 minutes for Vina silt loam, and 660 minutes (11 hours) for Altamont adobe clay. Data illustrating the exit of water are plotted in figure 17. Here the textural differences are even more outstanding. Generally speaking the heavier the texture of the soil—the higher its content in clay—the more slowly the water penetrates. This is, however,

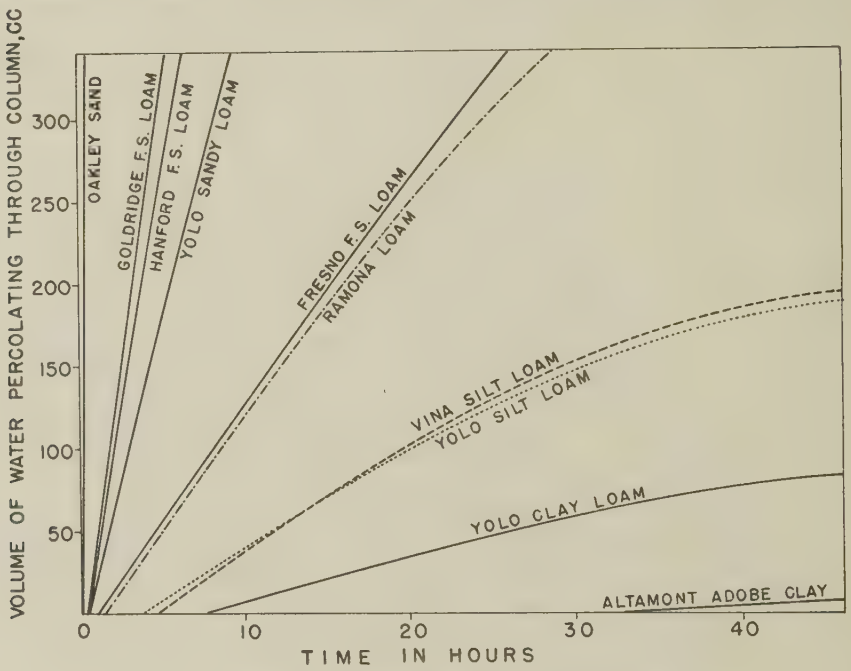


Fig.17.—Percolation of distilled water in relation to soil texture.

a general rule rather than a strict relation, for the Aiken soils are outstanding exceptions. Aiken clay (not shown in graph) behaves much like Hanford fine sandy loam, and Aiken clay loam like Fresno fine sandy loam. In all probability the chemical nature of the Aiken clay (kaolinitic clay minerals) and the relative coarseness of the colloidal particles account for this behavior.

Infiltration and Percolation of NH_4 Solutions.—It would consume too much space to present the corresponding graphs for all the solutions of NH_4OH and $(NH_4)_2SO_4$ that were investigated. One example may suffice to bring out the pertinent relations. Figure 18 shows the entry of $(NH_4)_2SO_4$ and NH_4OH solutions of various strengths into a Yolo clay loam. As compared with distilled water alone, the presence of $(NH_4)_2SO_4$ markedly increases the rate of penetration. This beneficial behavior is the more pronounced at the higher concentrations of $(NH_4)_2SO_4$. Ammonia, on the other hand, does not produce such striking effects. The rate of entry of NH_4OH solutions is slightly less than that of distilled water. Very similar relations were obtained for the percolation rate.

Figure 18, of course, applies to a specific soil only—namely, a representative of Yolo clay loam. Other soils behave differently. With Hanford fine sandy loam, all curves lie close together; this indicates that both NH_4OH and $(NH_4)_2SO_4$ exert a negligible influence on infiltration and percolation of water. The Aiken series suffers a marked reduction in permeability in the presence of NH_4OH.

These studies are summarized in table 2 and in figure 19. Table 2 shows (in cc) the volume of solution that percolates through a tube in 10 hours. For

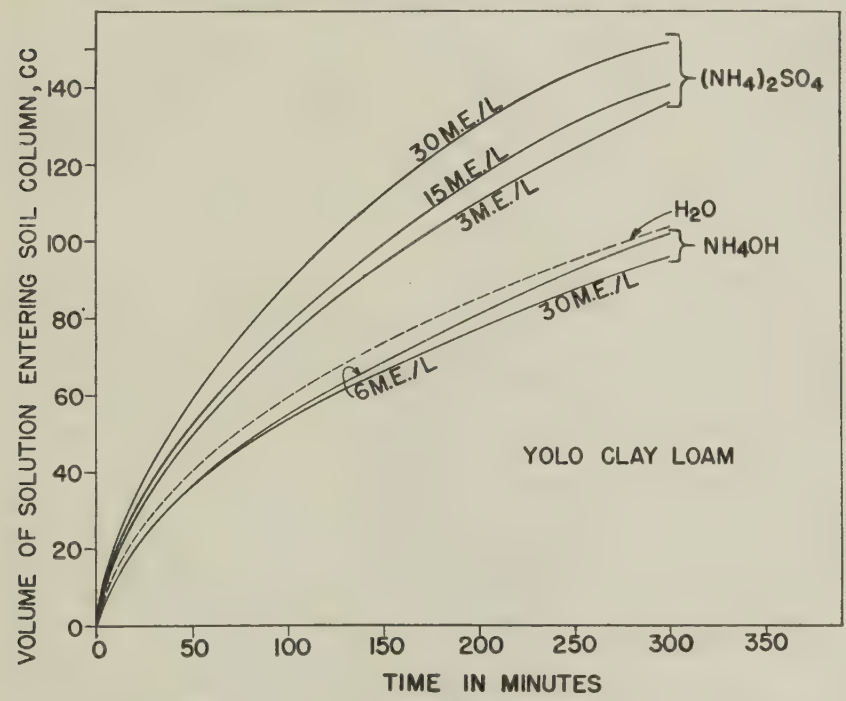


Fig. 18.—Effect of NH_4OH and of $(NH_4)_2SO_4$ upon the entry of solutions into Yolo clay loam.

each soil the beginning of this 10-hour period was made to coincide with the emergence of the first drop of percolate at the bottom of the tube. According to figure 17 the percolation during the first day is very nearly a straight-line function of the time, so that the values in table 2 may be used to calculate hourly percolation rates. Table 2 also contains the percolation rates of the solutions relative to distilled water. In figure 19 the various soil types are arranged according to decreasing rates of NH_4OH percolation. As may be readily seen, the rate of percolation of the $(NH_4)_2SO_4$ solution exceeds that of distilled water in all soils except Aiken clay loam. This improvement in penetration is especially conspicuous for the heavier soils of the montmorillonitic clay group, a behavior that might be anticipated on theoretical grounds. As is well known, $(NH_4)_2SO_4$ has high flocculating powers and thereby increases the state of aggregation of the colloidal clay particles. In consequence

TABLE 2

VOLUME OF OUTGOING SOLUTION DURING A PERIOD OF 10 HOURS

Soil type	Distilled water	$(NH_4)_2SO_4$ (15 milli-equivalents per liter)	NH_4OH (15 milli-equivalents per liter)	Percolation relative to distilled water	
				$(NH_4)_2SO_4$	NH_4OH
	cc	*cc*	*cc*	*ratio*	*ratio*
Oakley sand	5,600	6,700	6.100	1.20	1.09
Goldridge fine sandy loam	684	716	596	1.05	0.87
Hanford fine sandy loam	606	680	606	1.12	1.00
Aiken clay	590	650	220	1.10	0.37
Yolo sandy loam	396	480	360	1.21	0.91
Aiken clay loam	150	145	133	0.97	0.89
Fresno fine sandy loam	140	190	150	1.36	1.07
Ramona loam	140	180	140	1.29	1.00
Yolo silt loam	75	125	80	1.67	1.07
Vina silt loam	68	88	78	1.29	1.15
Yolo clay loam	25	48	25	1.92	1.00
Altamont adobe clay	5	19	6	3.80	1.20

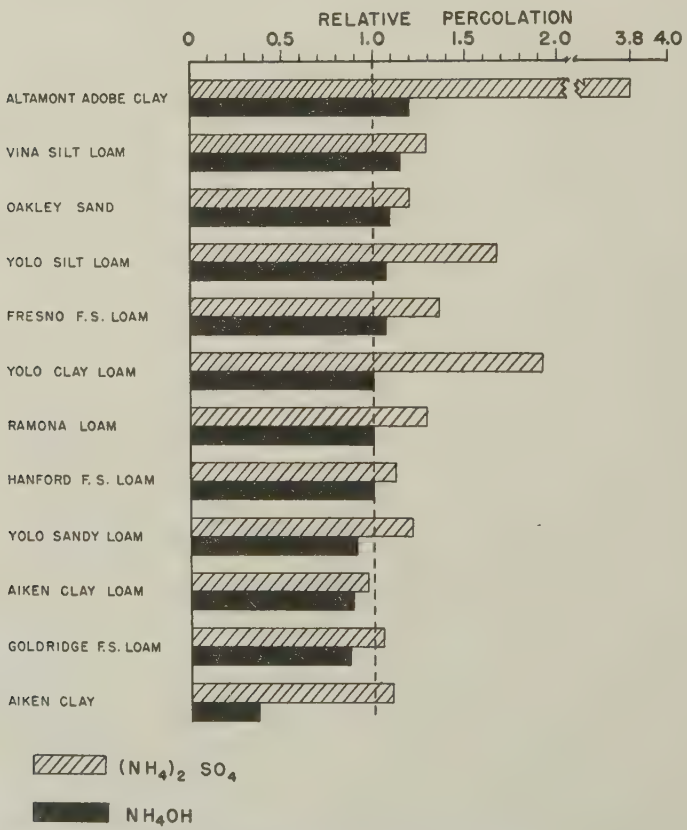


Fig. 19.—Relative percolation of NH_4OH and $(NH_4)_2SO_4$ in comparison with distilled water. The bars that extend beyond 1.0 indicate soils in which the solution penetrated better than distilled water.

the pore space of the soil tends to become larger, and the passage of the water molecules easier. The results obtained with NH_4OH solutions present a more complicated picture. The soils on the upper portion of the vertical axis exhibit slight improvement in penetration when NH_4OH is applied, whereas the last four show a diminishing effect as contrasted with distilled water. The latter feature is most conspicuously manifested in Aiken clay.

In contrast to $(NH_4)_2SO_4$, which is a strongly flocculating agent, NH_4OH may also act as a dispersing medium. This latter quality is especially conspicuous in acid soils. Addition of NH_4OH to such soils neutralizes the acidity, as indicated on page 442. The resulting NH_4-clay possesses a higher zeta potential than the original H-clay, and dispersion of the clay particles takes place. The effective pore size tends to be reduced, and the percolation of water is slowed.

TABLE 3

RELATIVE PERCOLATION RATES OF DISTILLED WATER INTO AMMONIATED AND NONAMMONIATED SOILS

Soil type	Soil treatments before measurement		
	H_2O	$(NH_4)_2SO_4$	NH_4OH
Yolo clay loam	1.00	0.96	1.17
Vina silty loam	1.00	.67	1.10
Aiken clay	1.00	.61	0.34
Ramona loam	1.00	.37	1.29
Yolo silty clay loam	1.00	0.31	1.04

Water Penetration Subsequent to Ammonia Treatments.—Irrigating a soil that has been previously treated with NH_4 solutions will remove free electrolytes, and changes in rates of water percolation are likely to ensue. These were studied in conjunction with the percolation experiments already mentioned.

Soil columns were leached with $(NH_4)_2SO_4$ and NH_4OH solutions in concentrations and amounts used in irrigation practice. Corresponding sets of columns were leached with distilled water only. After treatment all soils were allowed to drain for 3 days. Infiltration and percolation rates of distilled water were then measured over a period of 200 hours. During the first few hours the infiltration rates closely corresponded to those of the NH_4 solutions; but as leaching continued, marked changes in rates were observed.

Table 3 summarizes the findings. It contains the percolation rates of distilled water into soils previously leached with NH_4 solution or with distilled water. Surprising is the fact that in all soils, except Aiken clay, the $(NH_4)_2SO_4$-treated soil has the poorest water penetration, whereas before leaching it had the best. (Compare fig. 19.) This suggests that removal of free electrolyte may produce significant dispersion of the $(NH_4)_2SO_4$-treated soil.

The time interval of 3 days between the end of the NH_4 treatment and the first measurements of water percolation was too short to permit significant nitrification. To ascertain the effect of nitrification on permeability, 700-gram lots of Yolo clay loam and Aiken clay loam were placed in shallow pans and moistened. A little water extract of a fertile garden soil was added to insure the presence of nitrifying bacteria. Two thirds of the pans each received 7.5

milliequivalents of $(NH_4)_2SO_4$ or NH_4OH. All soils were kept moist for 4 weeks and were then dried and screened through a 2-mm sieve. Soil columns 2 inches thick were prepared, and the rates of infiltration and percolation of distilled water were determined in the usual manner. Only traces of nitrate nitrogen were found in the leachate, although the ammonia nitrogen content of the soil was reduced by 50 per cent. Presumably this chemical had been consumed by microörganisms.

In the Aiken clay loam the rates of entry and percolation for 5 to 60 hours were highest for $(NH_4)_2SO_4$- and lowest for NH_4OH-treated soil. The sample not receiving nitrogen occupied an intermediate position. In the Yolo clay loam a similar sequence was obtained for the initial infiltration period, but after 10 to 40 hours all NH_4-treated soils had only about one half the percolation velocity of the untreated soil.

To summarize, these experiments indicate that soils fertilized with ammonium compounds may eventually suffer a reduction in rates of water percolation. Many field observations on heavy applications of ammonium sulfate support these laboratory findings.

GENERAL DISCUSSION

Considerable controversy exists regarding the comparative merits of Agricultural Ammonia and $(NH_4)_2SO_4$ as a nitrogen fertilizer. The farmer usually asks, "Which of the two fertilizers is better?" His inquiry can be answered only by long-time experiments involving crop yields and economic considerations; the problem lies beyond the scope of the present investigation. Several controversial questions relating to the indirect effects on crop production may, however, well be discussed in the light of these studies (*8*).

Promoters of Agricultural Ammonia emphasize that their product does not contain anions, such as sulfate or chloride, which might remain in the soil solution as a residue. Theoretically, continued use of large amounts of $(NH_4)_2SO_4$ might ultimately increase the sulfate and sulfuric acid concentration of the soil solution to such an extent as to injure plant growth. In practice, however, such conditions are not very common. Winter rains and occasional heavy irrigations will displace the concentrated soil solutions to greater depth, beyond the reach of most roots. Since, moreover, soils usually contain some exchangeable calcium, the $(NH_4)_2SO_4$ will be converted into NH_4-clay and $CaSO_4$. The latter salt is sparingly soluble, yielding (at saturation) a sulfate concentration of 30 to 35 milliequivalents per liter, which is not known to be toxic to common crops.

Ammonia dissolved in water becomes NH_4OH. It is a weak base and therefore slightly alkaline, having a theoretical pH value of about 10.8 at a concentration of 10 milliequivalents of NH_4OH per liter (170 p.p.m. NH_3). Under field conditions, because of the pressure of CO_2, the reaction is less alkaline. In soils containing exchangeable calcium the addition of NH_4OH will produce NH_4-clay and $Ca(OH)_2$, resulting in a further increase in pH. Locally, unfavorable effects may occur—for example, the precipitation of phosphates and of micronutrients such as zinc. As soon as the ammonia is nitrified, the alkaline reaction will disappear; but not necessarily all the precipitates, since these may be irreversible.

According to some claims, ammonia liberates from the soil substantial amounts of plant foods, especially potash and phosphate. As far as exchangeable potassium is concerned, this claim is well substantiated by the present study. However, $(NH_4)_2SO_4$ is more effective in this respect than Agricultural Ammonia. Since potassium held on the clay in exchangeable form is readily taken up by roots, the release of exchangeable potassium by NH_4 is probably less important in plant nutrition than has hitherto been assumed. According to some growers, NH_4 liberates not only exchangeable potassium, but also a "nonexchangeable" kind, which presumably is locked up in the interior of mineral particles. Such an assertion is not easy to verify.

Ammonia, owing to its alkaline reaction, may possibly release phosphate from those lateritic soils (for example, the Aiken series) in which PO_4 occurs as phosphated kaolinitic clays, or as iron and aluminum phosphate. In many California soils, on the other hand, phosphate exists as calcium phosphate, whose solubility becomes less as the alkalinity becomes greater. In these soils NH_3 would, temporarily at least, adversely affect the availability of phosphate. In contrast to NH_4OH, the reaction of $(NH_4)_2SO_4$ is slightly acid (pH = 5.7 for a concentration of 10 milliequivalents per liter); and its effect on phosphate availability should therefore be opposite to that of ammonia. One would expect $(NH_4)_2SO_4$ to lower the availability of phosphate in lateritic soils and to increase it in soils containing calcium phosphate.

"Wherever the water goes the ammonia goes" is another claim frequently advertised. The present study conclusively shows, however, that water and ammonia may move independently of each other. Yet the counterstatement that NH_3 is always fixed in the first 2 or 3 inches of soil is likewise erroneous. Actually, the depth of NH_3 penetration is conditioned to a high degree by soil texture. In coarse-textured soils (sands) NH_3, in the amounts used in irrigation agriculture, distributes itself rather uniformly through a depth exceeding 6 inches, whereas in fine-textured soils (clay loam and clays) practically all the NH_3 is fixed in the top 2 inches. With respect to penetration, NH_3 and $(NH_4)_2SO_4$ behave very much alike, though in acid soils $(NH_4)_2SO_4$ penetrates deeper than NH_4OH.

The soil structure must also be considered. Fine-textured soils of the adobe type form wide and deep cracks upon drying. Conceivably, irrigation water that fills these cracks and crevices may carry some of the dissolved NH_3 to considerable depth.

"Ammonia has a very marked effect in causing soil colloids to coagulate so that heavy soils which allow only little penetration of water gradually become lighter and allow better penetration." Again, this statement is true in part. First of all, the coagulating effect of hydroxides is manifested primarily in base-saturated soils—that is, soils having neutral or alkaline reaction. Second, in acid soils monovalent hydroxides tend to have a dispersing or deflocculating effect. The data obtained in this study fully confirm both the coagulating and the dispersing effect for ammonia. NH_4OH increases water penetration in some soils, decreases it in others, as compared with distilled water. In all tests performed, $(NH_4)_2SO_4$ proved to be a superior coagulator. Fortunately, owing to the ultimate utilization of nitrogen by plants, the reduction in penetration observed in some soils need not be cumulative and permanent.

Generally speaking, in their principal behavior in the soil, NH_3 and $(NH_4)_2SO_4$ are similar. Each has certain advantages and disadvantages; but as far as the soil is concerned, apparently neither is more beneficial than the other.

SUMMARY

Laboratory studies on the behavior of NH_3 (or NH_4OH in water) and $(NH_4)_2SO_4$ in soils revealed the following facts:

1. The uptake of nitrogen in soil suspensions containing NH_3 and $(NH_4)_2SO_4$ is, broadly speaking, a function of soil texture. Fine-textured soils adsorb more nitrogen than coarse-textured ones. Numerous exceptions, however, exist, being conditioned by soil acidity and by other factors such as the nature of the clay minerals.

2. Under comparable conditions, acid soils tend to adsorb more nitrogen from NH_4OH than from $(NH_4)_2SO_4$. Alkaline soils, as a rule, adsorb more nitrogen from $(NH_4)_2SO_4$ than from NH_4OH.

3. Determinations of the depth to which NH_4 compounds penetrate in artificially prepared soil columns for a 10-inch irrigation containing 127 p.p.m. of nitrogen indicate that (*a*) in Oakley sand, NH_4OH and $(NH_4)_2SO_4$ readily penetrate below a depth of 6 inches; (*b*) in Yolo sandy loam, penetration is restricted to a depth of 4 inches; (*c*) in Yolo clay loam, all nitrogen is held in the first 2 inches; and (*d*) in Aiken clay loam, $(NH_4)_2SO_4$ penetrates to greater depth (4 inches) than NH_4OH (2 inches).

4. The process of nitrogen adsorption is governed by base-exchange reactions. With $(NH_4)_2SO_4$ and NH_4Cl the exchange is equivalent. For every NH_4 ion adsorbed, a corresponding amount of cation is released. In NH_4OH the amount of NH_4 adsorbed greatly exceeds the number of bases liberated. Ammonia may react with hydroxyl ions of the clay lattice.

5. Ammonium ions readily displace exchangeable potassium ions from clay particles. The extent of this reaction is greatly influenced, however, by the degree of potassium saturation of the clay. For most soils the release of potassium by NH_4 fertilizers is probably of minor significance.

6. Dry clays readily adsorb NH_3 from vapors containing NH_3 molecules. These molecules are held loosely and may be easily removed by aeration.

7. Judging from experiments with excised plant roots, NH_4 adsorbed on clays can be readily utilized. Likewise nitrification of adsorbed NH_4 is easily accomplished.

8. The influence of NH_4 on water penetration in artificially prepared soil columns varies so greatly among different soils that no generalizations appear possible. The following trends, however, were observed: In 11 out of 12 soils, ranging in texture from sands to clays, the percolation rates of $(NH_4)_2SO_4$ solutions were higher than those of distilled water. The influence of NH_4OH solutions was much more variable. In 5 soils NH_4OH improved water percolation as compared with distilled water; in 3 soils NH_4OH had no effect; and in 4 soils it lowered the percolation rates. This decrease was most pronounced in Aiken clay, an acid soil containing kaolinitic clay minerals.

9. In soils that have been treated with NH_4 compounds, the subsequent penetration rate of distilled water may suffer a reduction, especially in the case of $(NH_4)_2SO_4$.

LITERATURE CITED

1. Albrecht, W. A., and T. M. McCalla.
1937. Nitrification of ammonia adsorbed on colloidal clay. Soil Sci. Soc. Amer. Proc. 2:263–67.

2. Bodman, G. B., and A. J. Mahmud.
1932. The use of the moisture equivalent in textural classification of soils. Soil Sci. 33:363–74.

3. Conrad, J. P.
1940. Retention by soils of the nitrogen of various compounds as shown by subsequent plant response. Jour. Agr. Res. 60:617–30.

4. Cornet, I.
1943. Sorption of NH_3 on montmorillonitic clay. Jour. Chem. Phys. 11:217–26.

5. Hardon, H. J.
1936. De afhankelijkheid van de adsorptie-capaciteit van bodemtype en bepalingswijze. Overdruk uit de Handelingen v/h. 7de Nederland. Indië Natuurw. Cong. 1936:601–12.

6. Hoagland, D. R., and T. C. Broyer.
1936. General nature of the process of salt accumulation by roots with description of experimental methods. Plant Physiol. 11:471–507.

7. Jenny, H., and A. D. Ayers.
1939. The influence of the degree of saturation of soil colloids on the nutrient intake by roots. Soil Sci. 48:443–59.

8. Rosenstein, L.
1936. Increased yields obtained from Shell Agricultural Ammonia (NH_3) in irrigated agriculture. Shell Chem. Co. Bul. 1:1–23.

9. Vanselow, A. P.
1932. Equilibria of the base exchange reactions of bentonites, permutites, soil colloids, and zeolites. Soil Sci. 33:95–113.